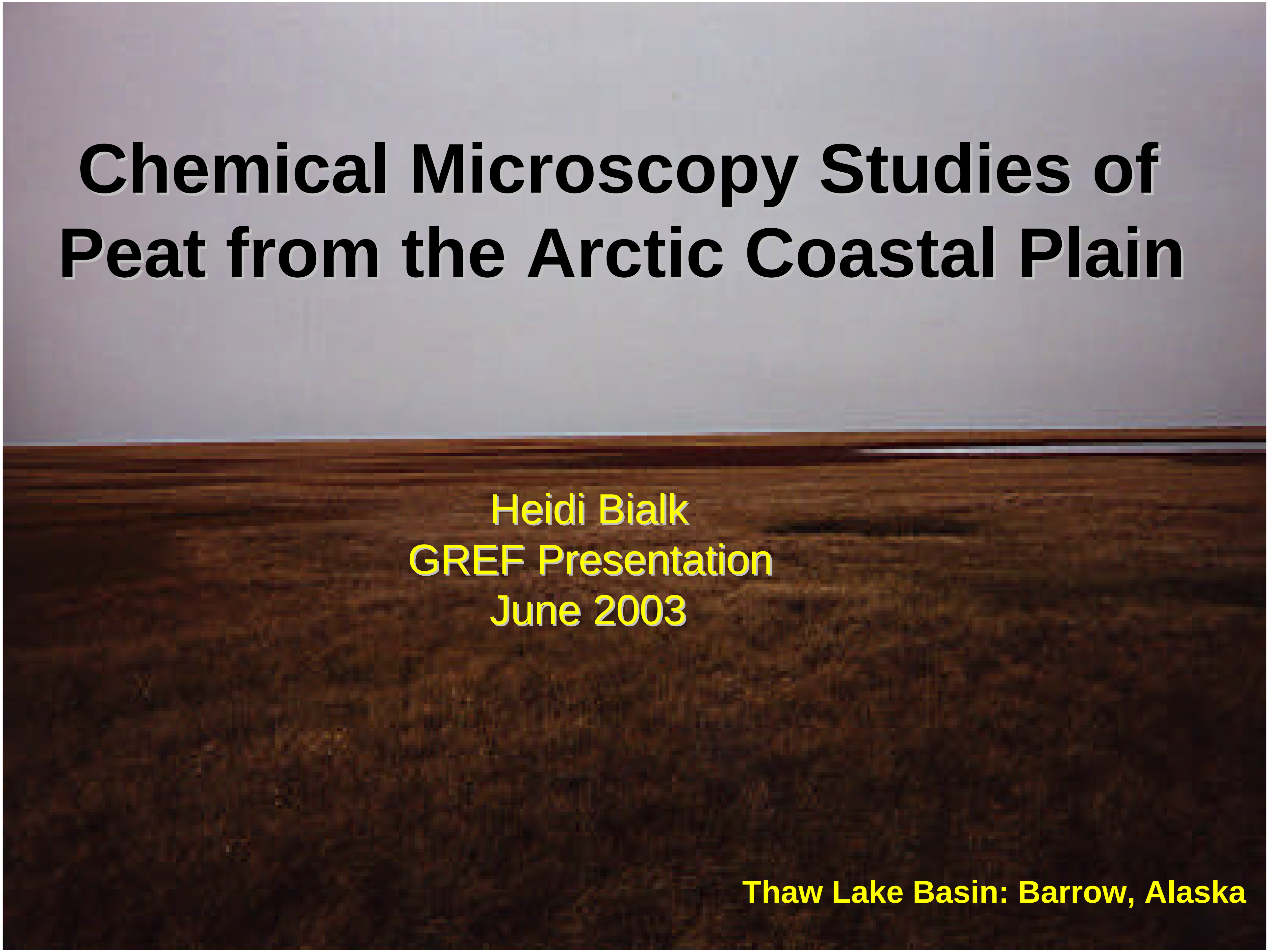
Chemical Microscopy Studies of Peat from the Arctic Coastal Plain

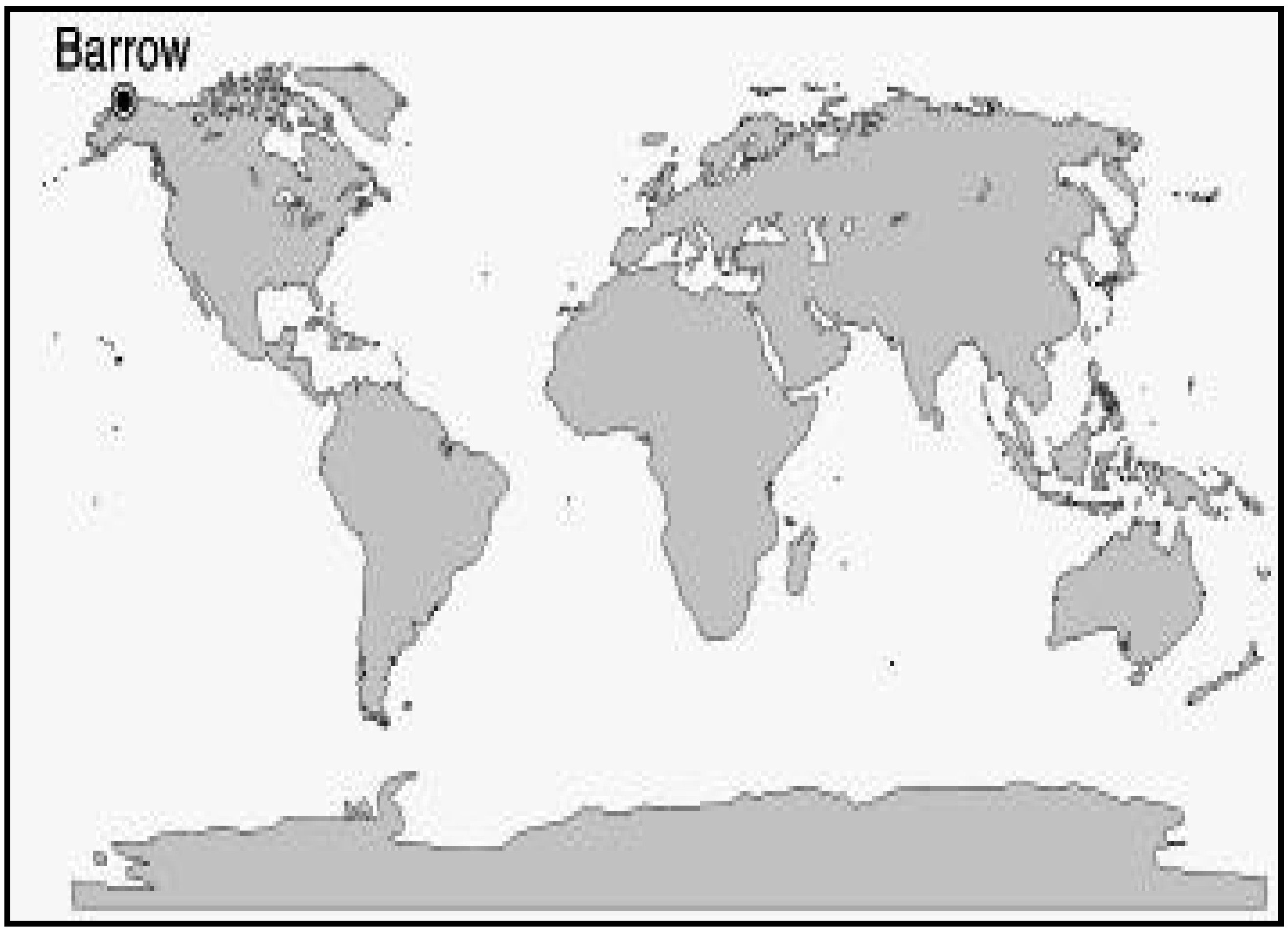


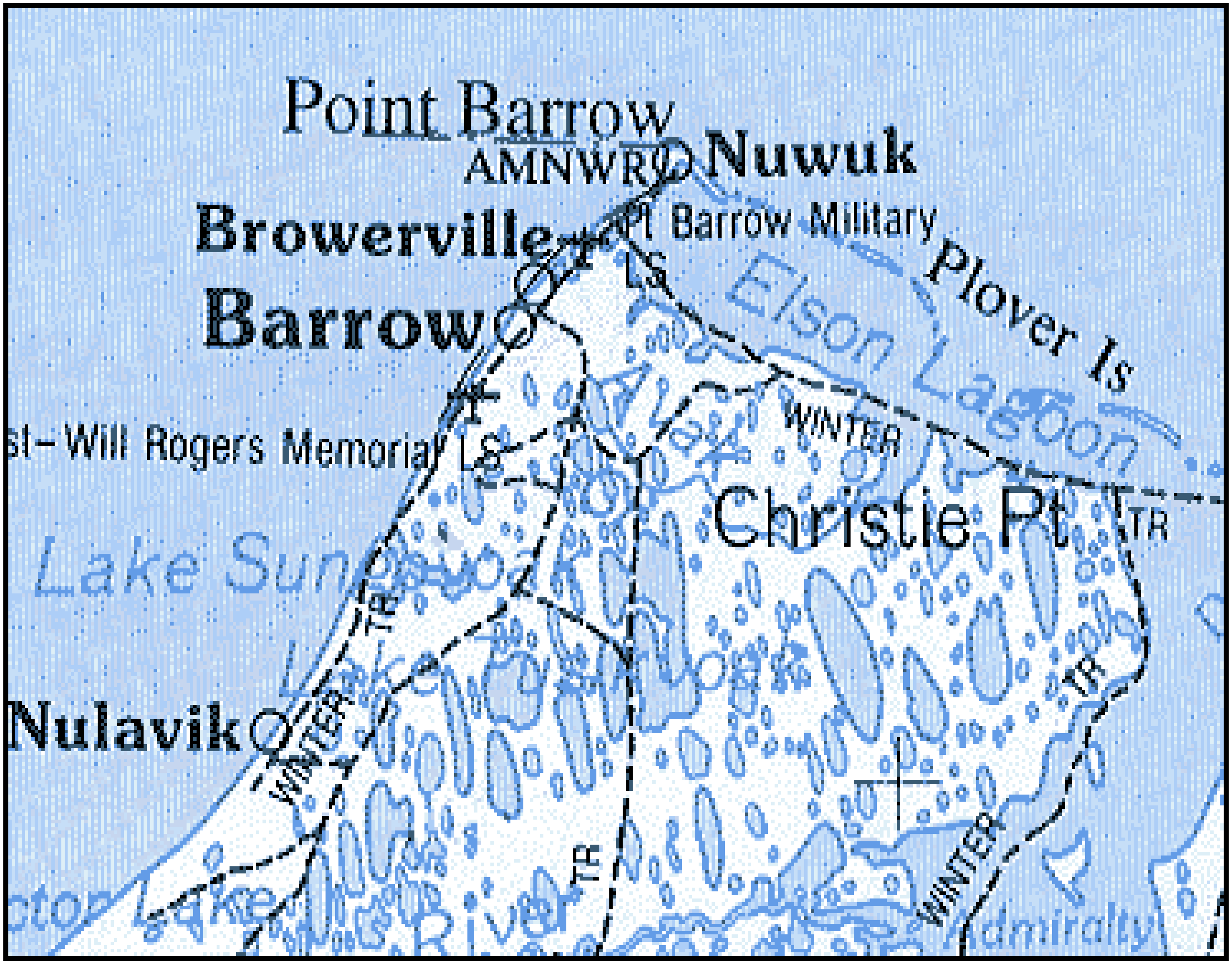
Heidi Bialk
GREF Presentation
June 2003

Thaw Lake Basin: Barrow, Alaska

Introduction

Portage, Alaska


Barrow



Point Barrow
AMNWR
Nuwuk
Browerville
Pt Barrow Military
LS
Barrow
Elson Lagoon
Plover Is
st-Will Rogers Memorial LS
WINTER
Christie Pt
TR
Lake Sungovoak
Nulavik
WINTER
TR
TR
WINTER
TR
WINTER
River
Admiralty


BARROW, ALASKA
DANGER!
Polar Bears

Overview

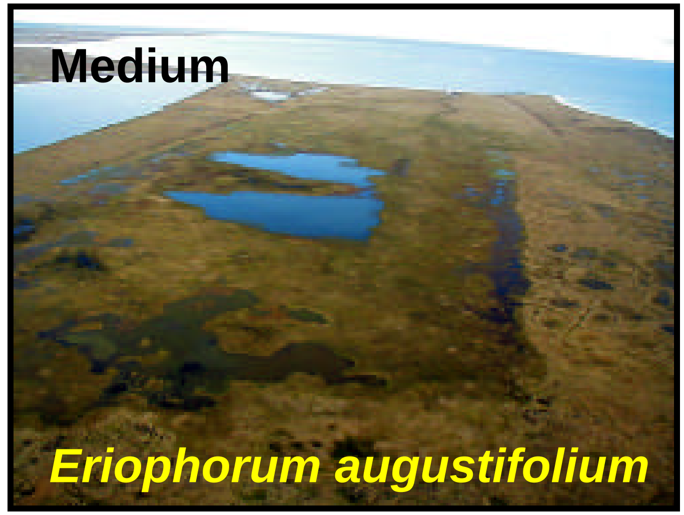
- **Introduction**
  - Background
- **Project Goals**
  - Objectives
  - Hypotheses
- **Experimental Methods**
  - Sample Collection and Sample Preparation
- **Preliminary Results**
  - Data Collection: XANES and Microscopy
  - Summary of Preliminary Results
- **Conclusions**
  - Future Directions
- **Acknowledgements**

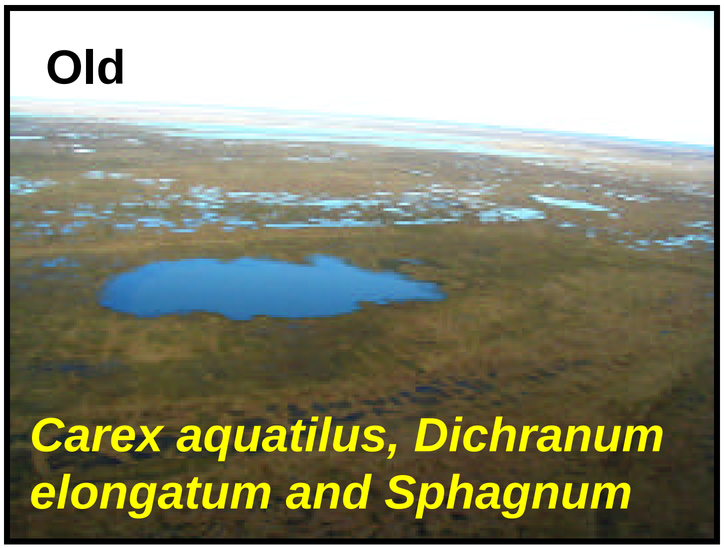
Whale Bone: Barrow, Alaska

Background: Why the Arctic Coastal Plain?

- Soils of the tundra biome are estimated to contain 13% of the world soil C pool
- Potential impact of climate warming on carbon accumulation in the arctic tundra has multiple scenarios.
- An improved understanding of the chemical nature of peat is needed in order to better predict impacts of climate change.

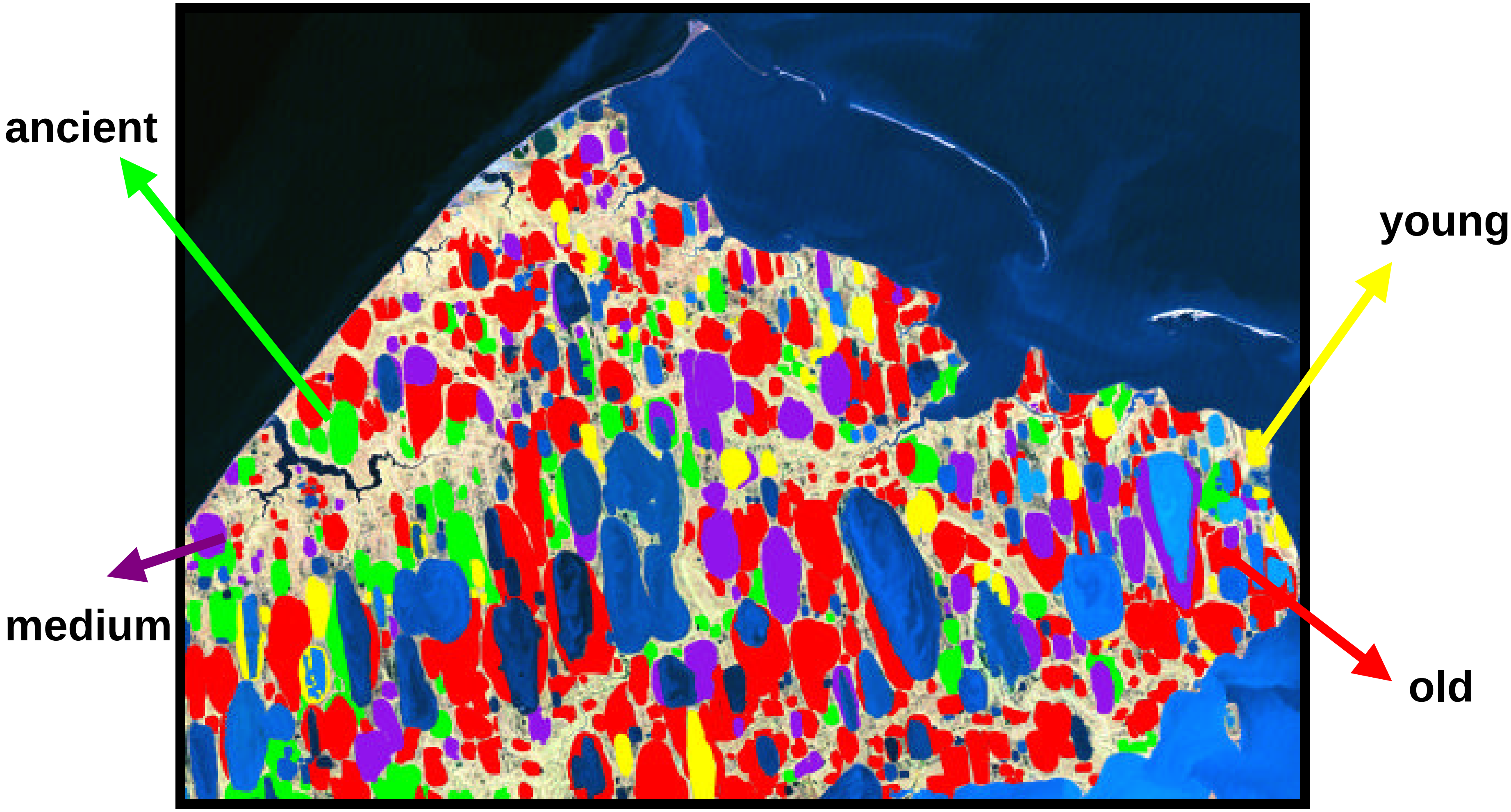
Age Classification of Basins





Photos by Dr. Wendy Eisner

Background Cont'd: Landsat-7 Imagery of the Coastal Plain



http://k2.gissa.uc.edu/~weisner/thawpage_files/frame.htm

Background Cont'd

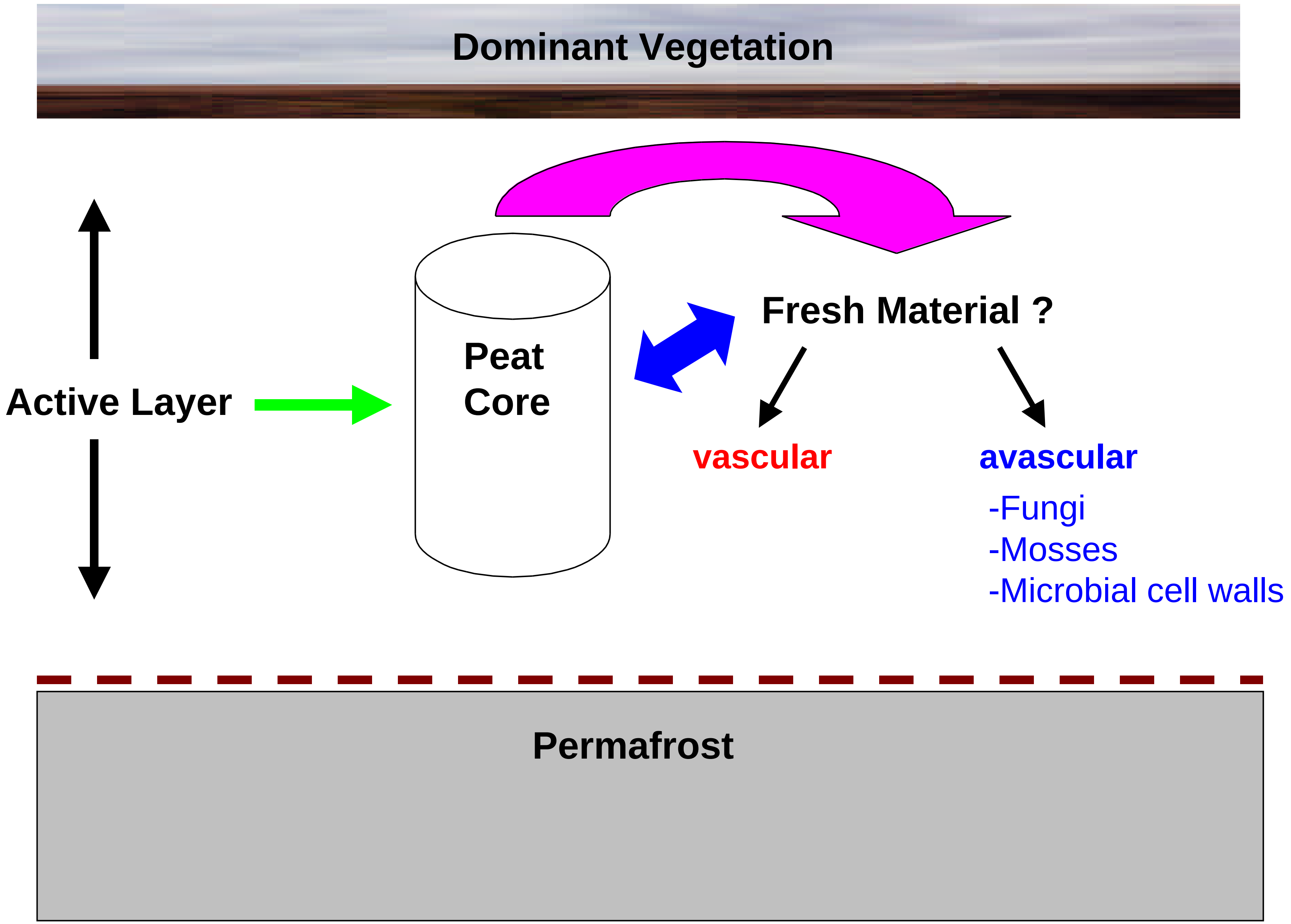
- There have been several studies on the progression of events within the thaw lake cycle (Billings and Peterson., 1980; Eisner., 1998a; Eisner and Peterson., 1998b).
- CPMAS-NMR used as a tool to characterize whole peat samples along with soluble extracts from the Arctic (Ping et al., 2001)
- Spectra do not reveal organic origins.
- Our approach will be similar, focusing on whole insoluble residues using synchrotron x-ray based methods that include microscopy.
   - chemical imaging

Project Goals

Alaskan Railroad: Anchorage, Alaska

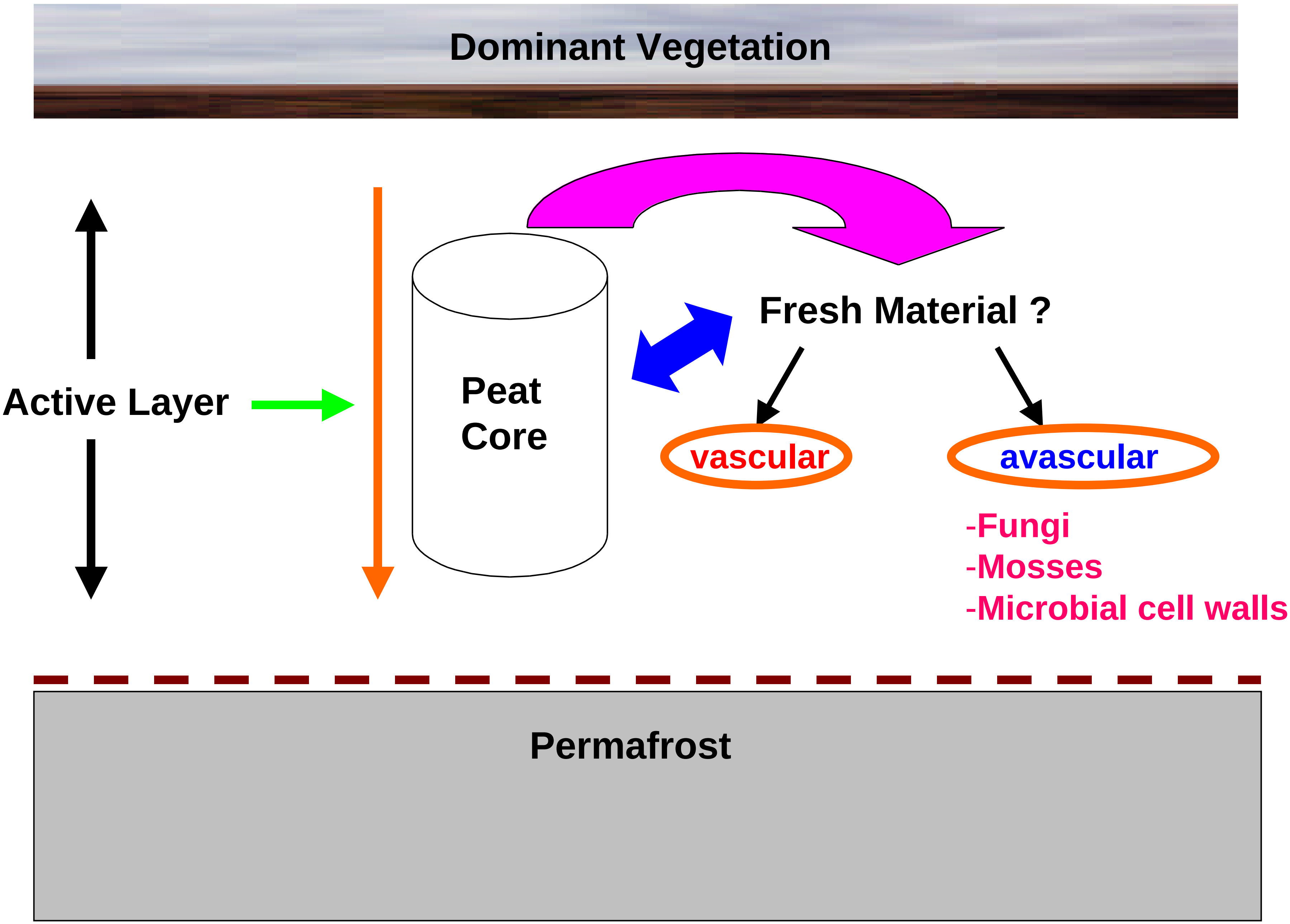
Objectives

- ❑ Bridge a gap in the current understanding of peat mats from the arctic coastal plain
- ➢ Quantify fresh source material in peat mats and assess the extent of decomposition
- ➢ Estimate the amount of chemically identifiable cell wall material of the following origin:
  - ✓ vascular plants through a chemical mapping based on lignin
  - ✓ moss, fungal, and microbial cell wall material


Dominant Vegetation
Active Layer
Peat
Core
Fresh Material ?
vascular
avascular
-Fungi
-Mosses
-Microbial cell walls
Permafrost

Main Hypotheses

- ❑ Chemical imaging will distinguish detritus of a vascular origin vs. detritus of an avascular origin via a chemical mapping of lignin. (Kogel-Knaber., 2002)
- ❑ There are chemical characteristics of fungal and bacterial cell wall material that will allow further distinction of detritus origin.
- ❑ Chemical imaging will reflect an increase in the degree of decomposition of detritus with depth. (Dai et al., 2001)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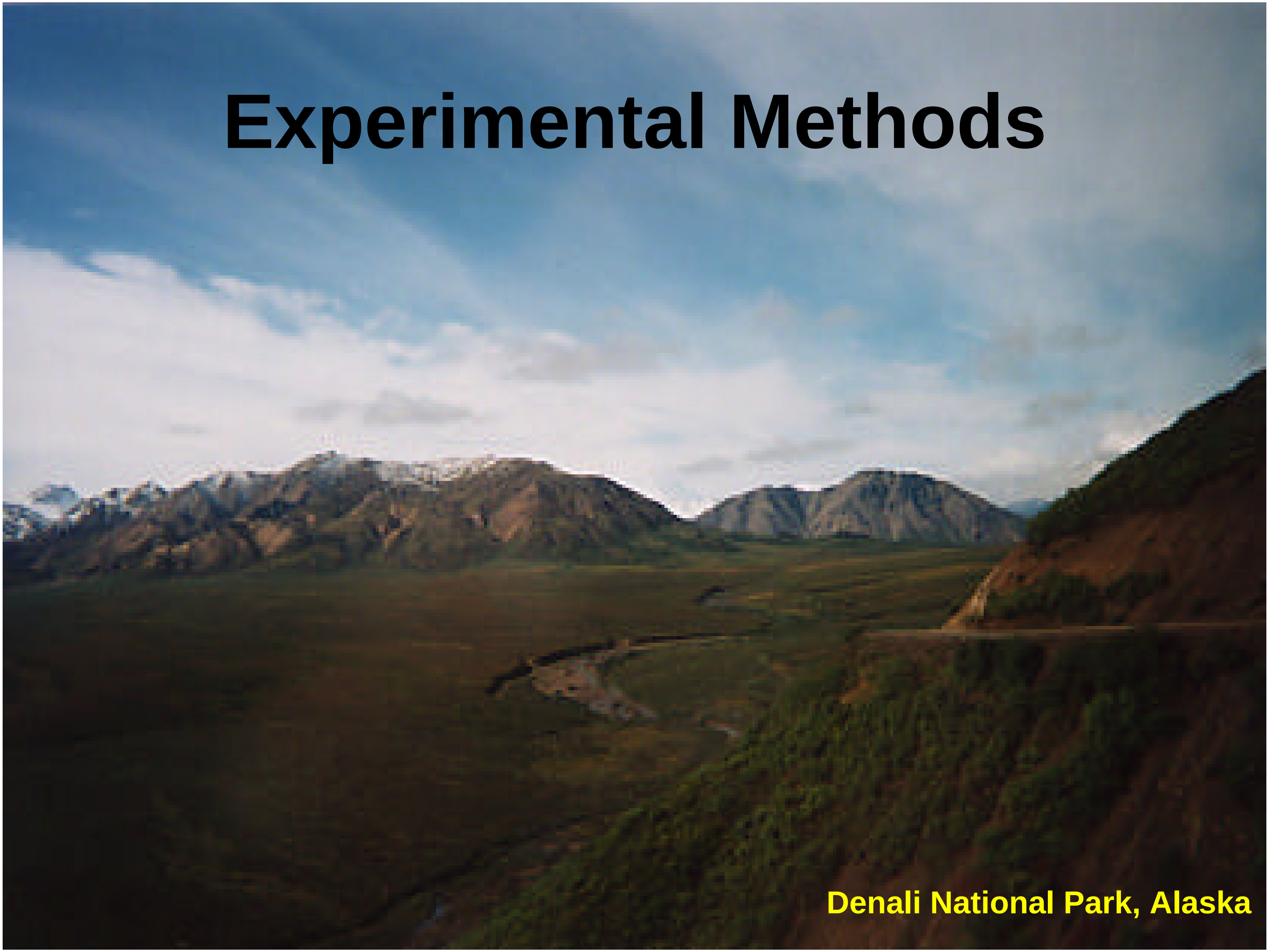
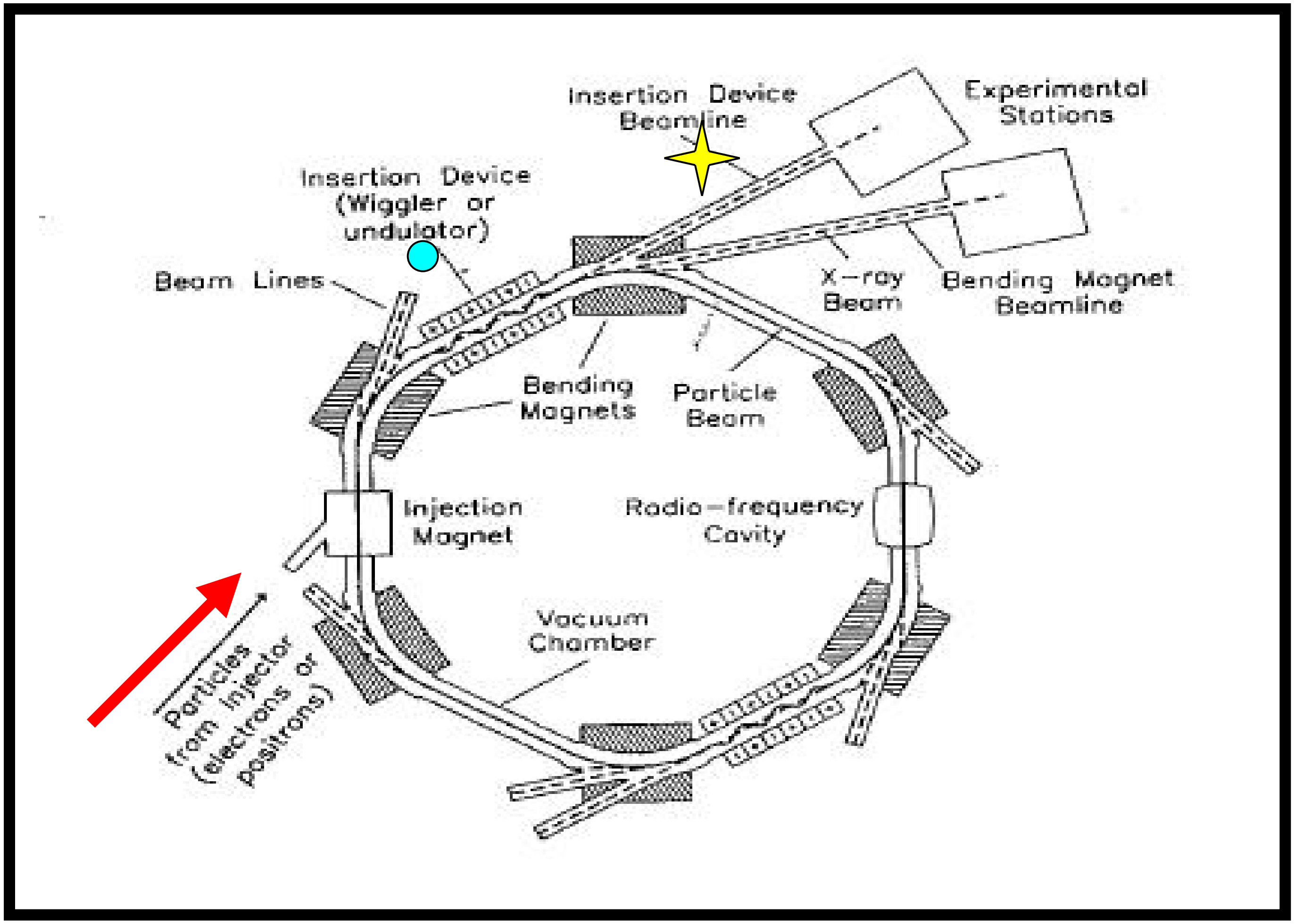
Experimental Methods



Denali National Park, Alaska

Synchrotron X-ray Radiation: What is it?

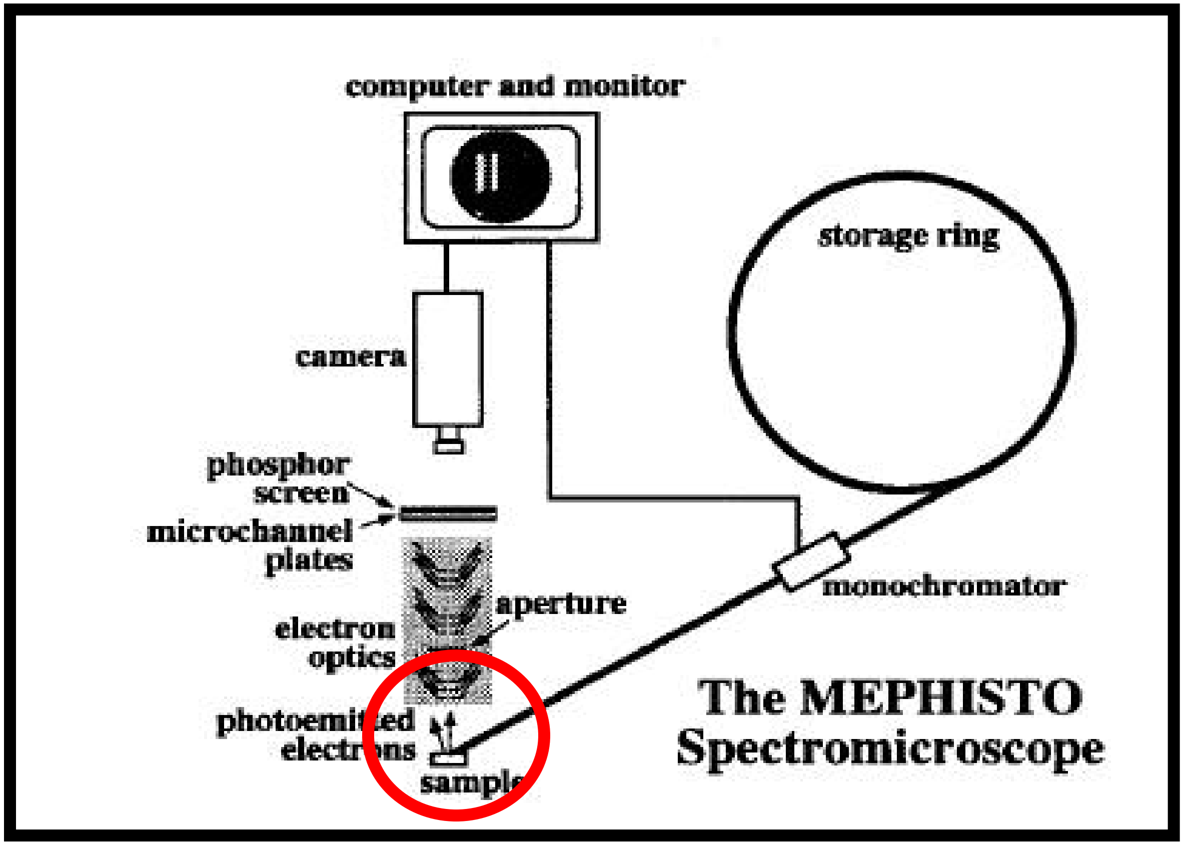


Synchrotron X-ray Analysis

Bulk XANES
Mark II Grasshopper
Port 103
Averages over an entire sample

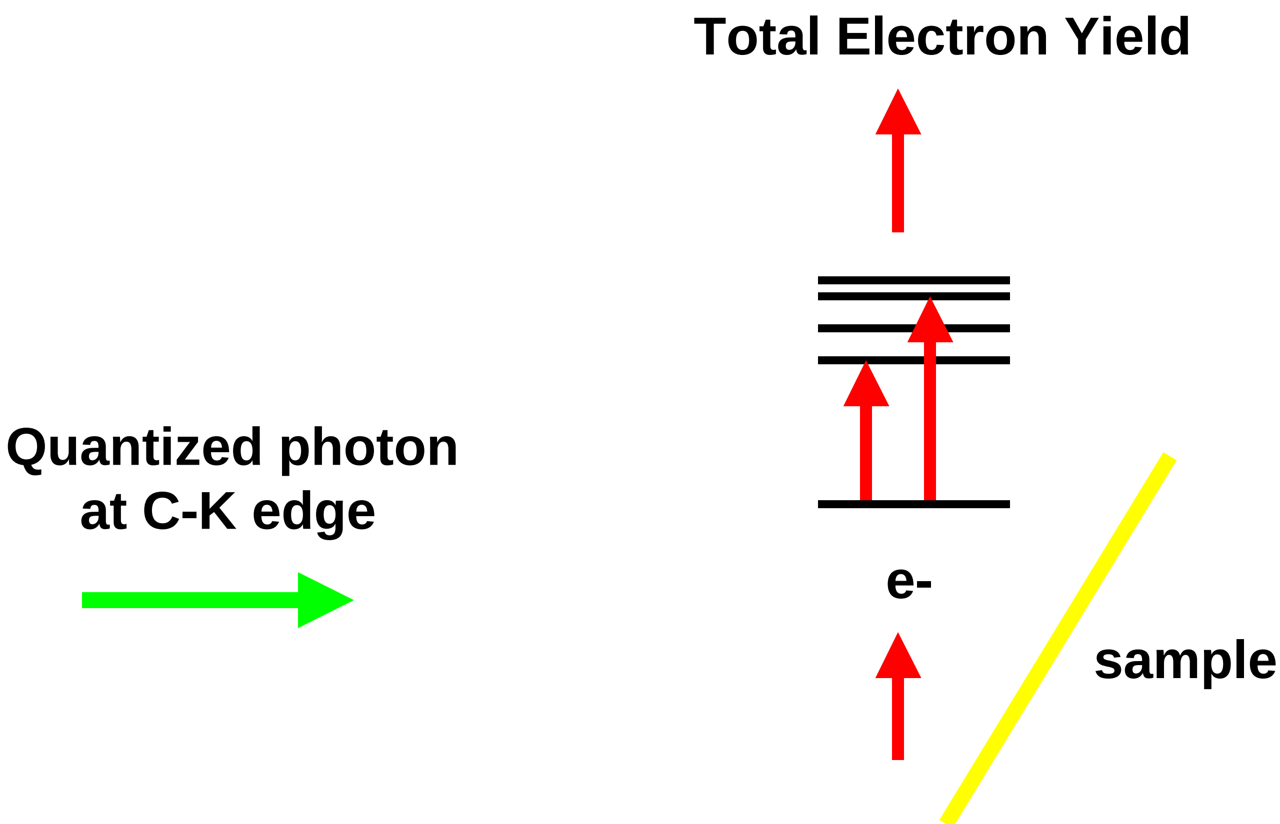
Chemical Microscopy
Mephisto
Selective Electronic Imaging

Schematic of Chemical Microscopy (Mephisto)

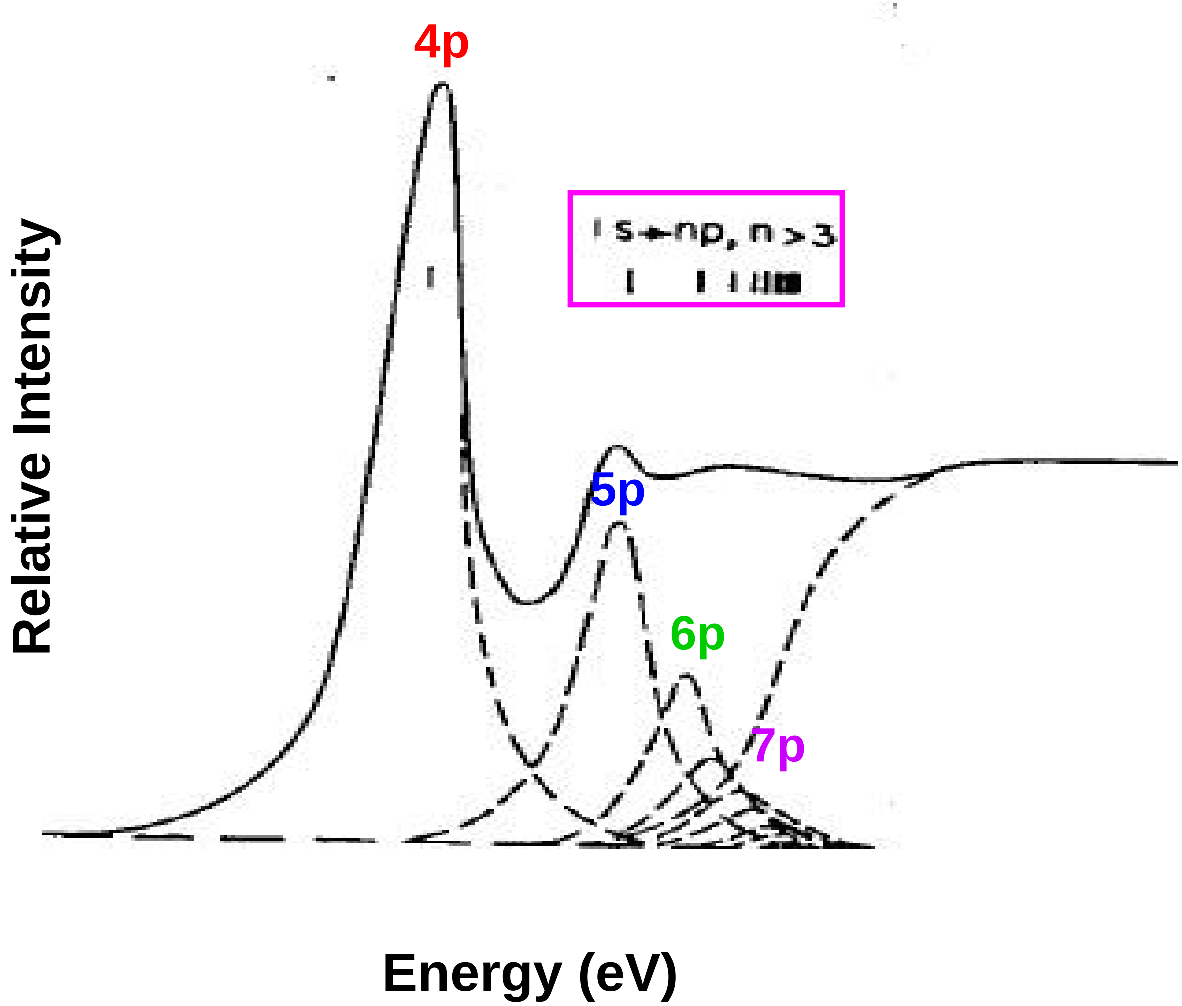


DeStassio et al., 1998

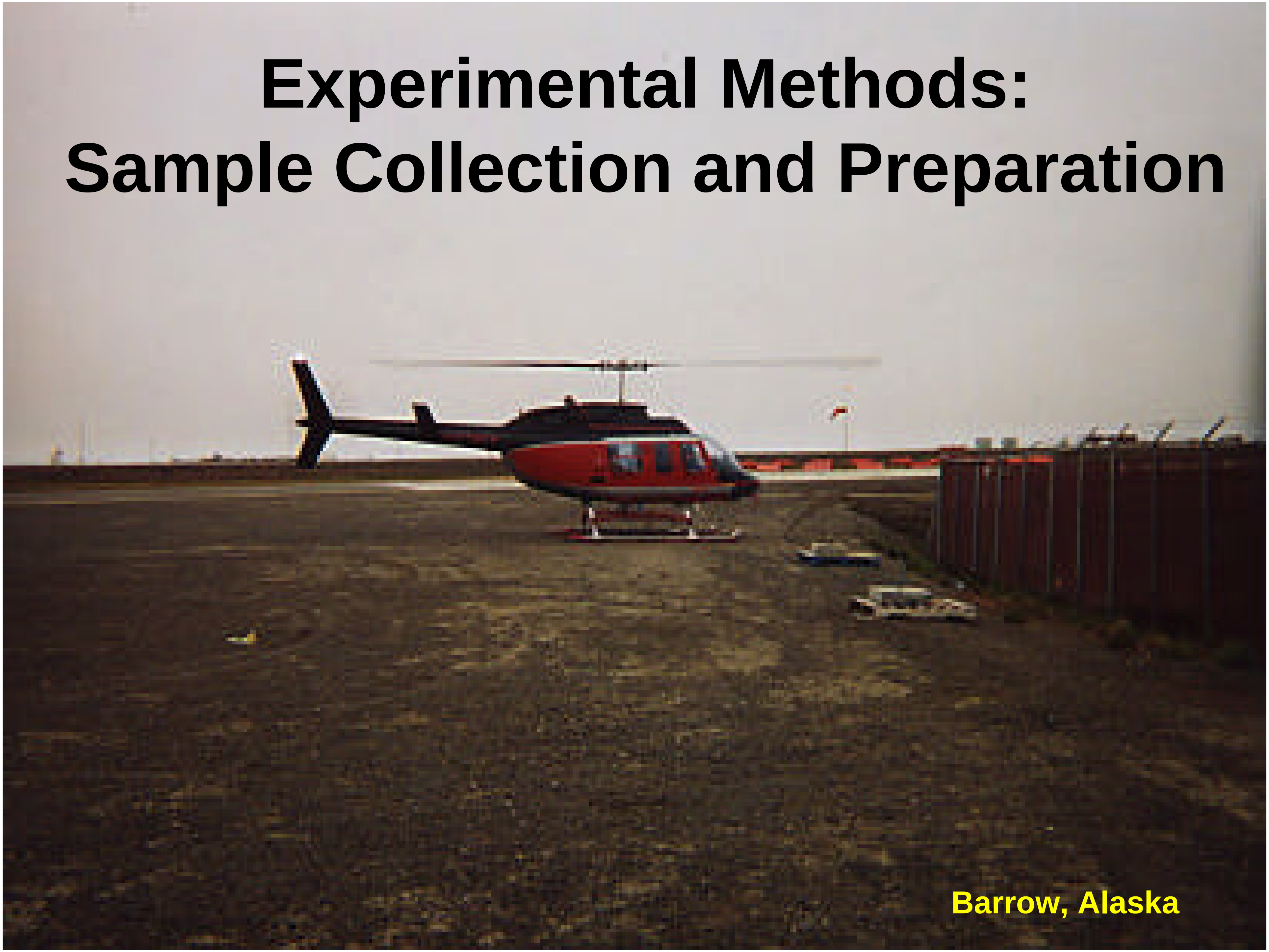
Brief Overview of X-ray Absorption



X-ray Absorption:
A Model Chemical Signature



Experimental Methods: Sample Collection and Preparation



Sample Collection: Vegetation

Table 1. Parent Vegetation from drained thaw lake basins in Barrow, Alaska, at 71 degrees N latitude

Lake Site	Age	Dominant Vegetation (other species present)
Footprint Lake Basin	young	***Arctophila fulva*** (graminoid), ***Caliergon*** (moss)
Golf Course Basin	medium	***Eriophorum augustifolum (***graminoid)
TC Basin	old	***Carex aquatilus*** (graminoid), ***Dichranum elongatum*** and ***Sphagnum*** (mosses)
RI Basin	ancient	***Eriophorum vaginatum*** (graminoid)

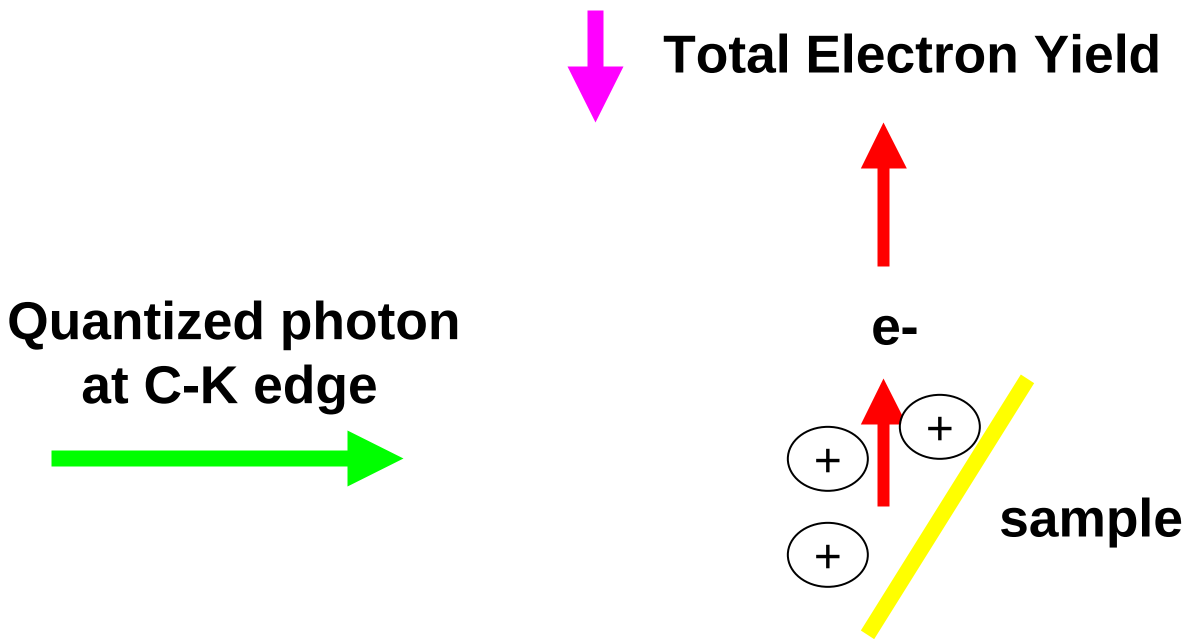
Sample Collection Cont'd

- ❑ **Peat Cores**

- ❑ **Microbial Cell Wall Isolation** (Dufrene et al., 1997; Dengis et al., 1995)
  - ➢ Bacteria: ***Archaea***

http://k2.gissa.uc.edu/~weisner/thawpage_files/frame.htm

Rationale for Sample Preparation



Sample Preparation

❑ **Soft X-ray Analysis in Bulk Mode** (Port 103)

- Samples ground and embedded into indium foil
- Coated with a 7 angstrom Pt-Pd alloy film
- Eliminates charging

❑ **Soft X-ray Analysis in Microscopic Mode**

- Samples fixed in a Polybed-812 & Spurr's carbon based resin
- Sectioned to 8 micrometers to minimize sample charging
- Smooth sample required for quality imaging

Sample Preparation: Microscopy

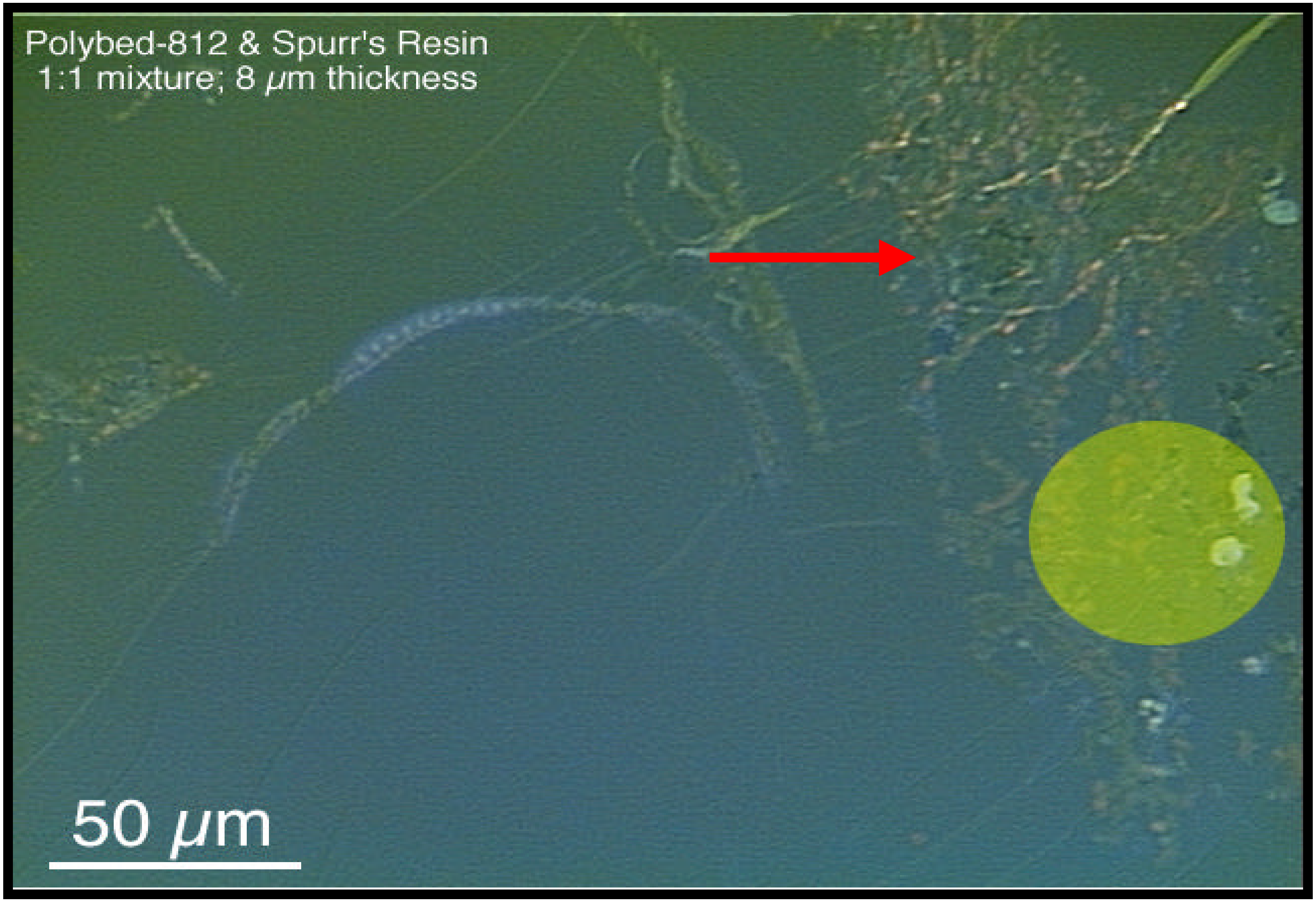
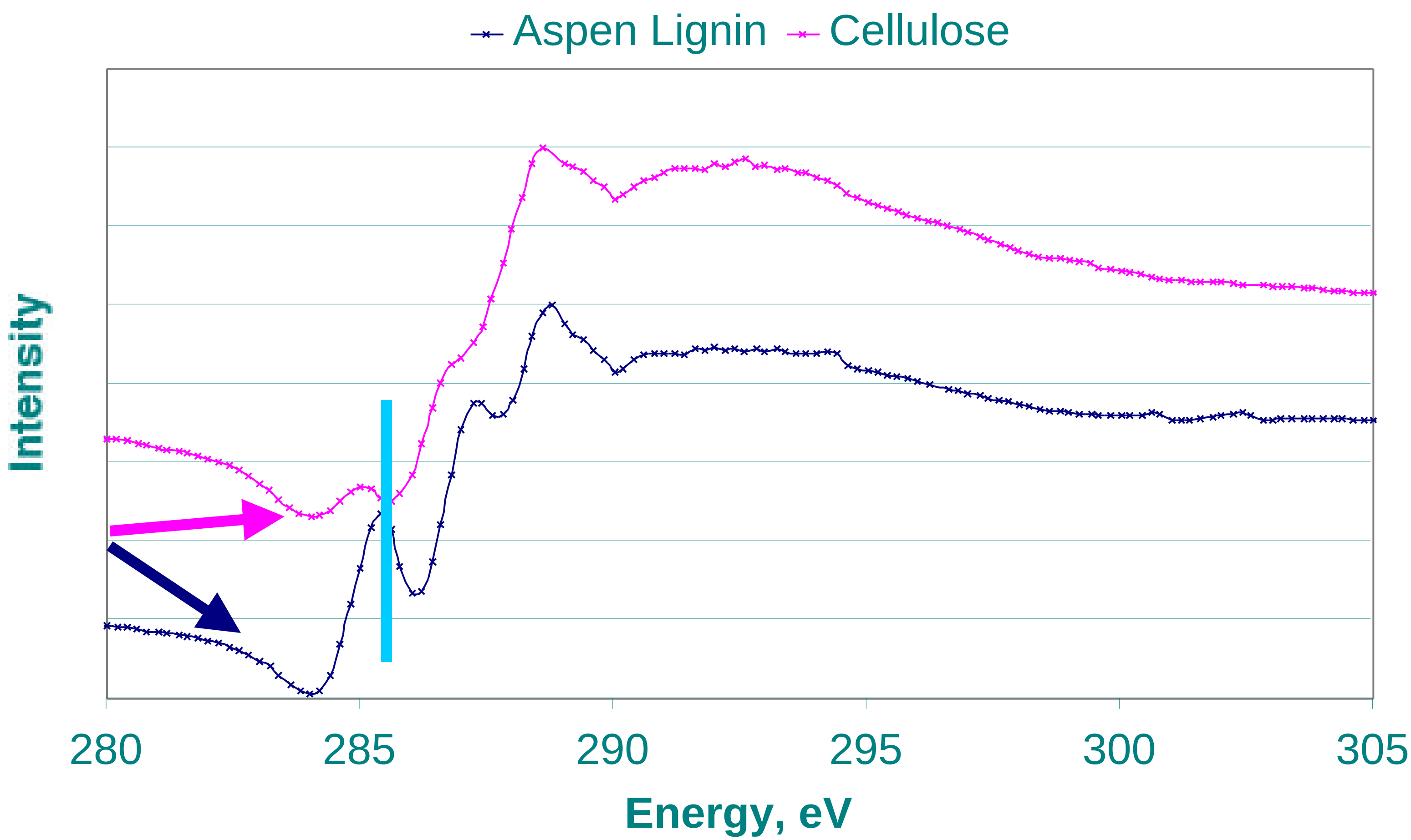


Photo by Russ Spears

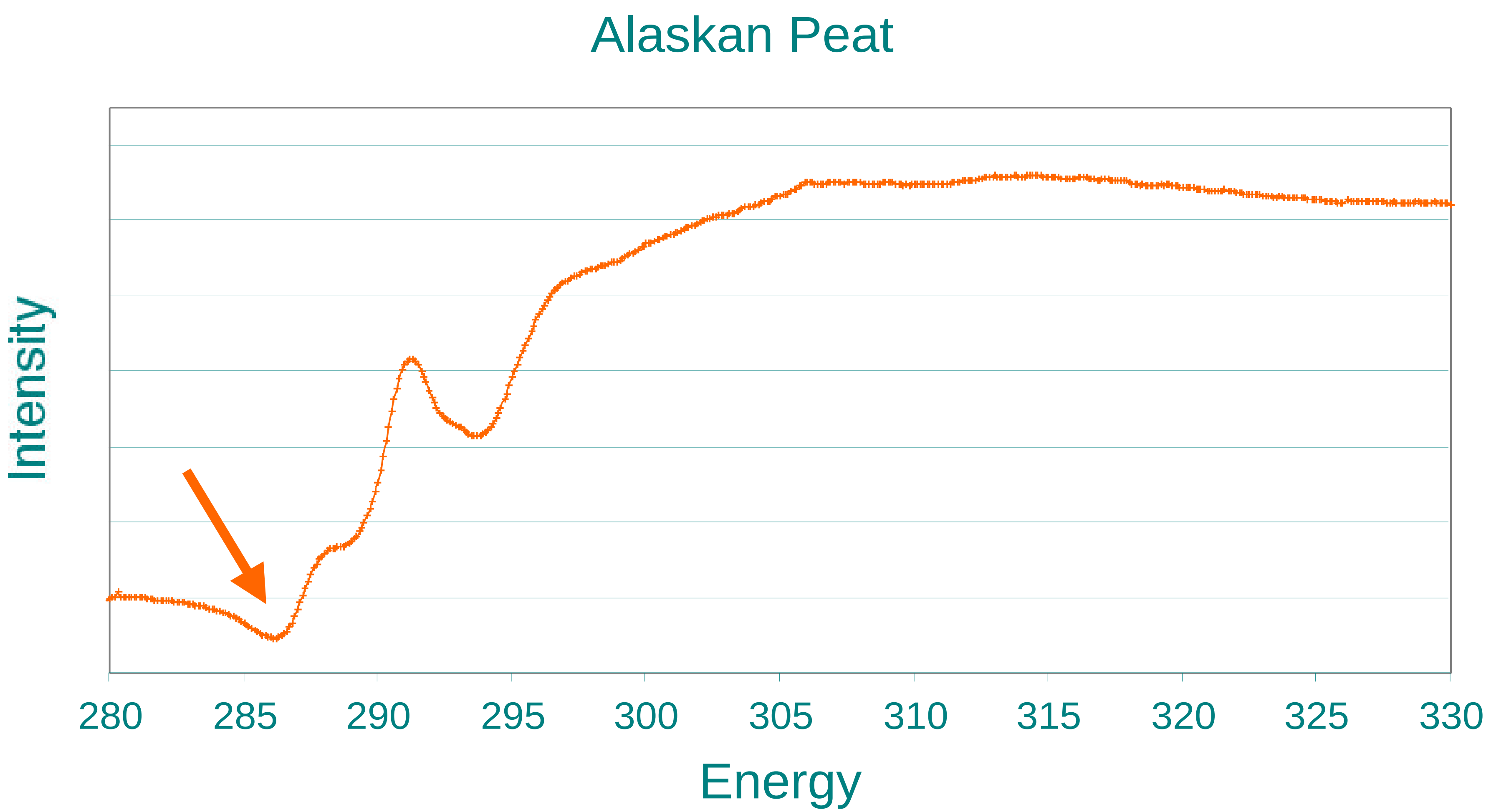
Preliminary Results

Denali National Park, Alaska

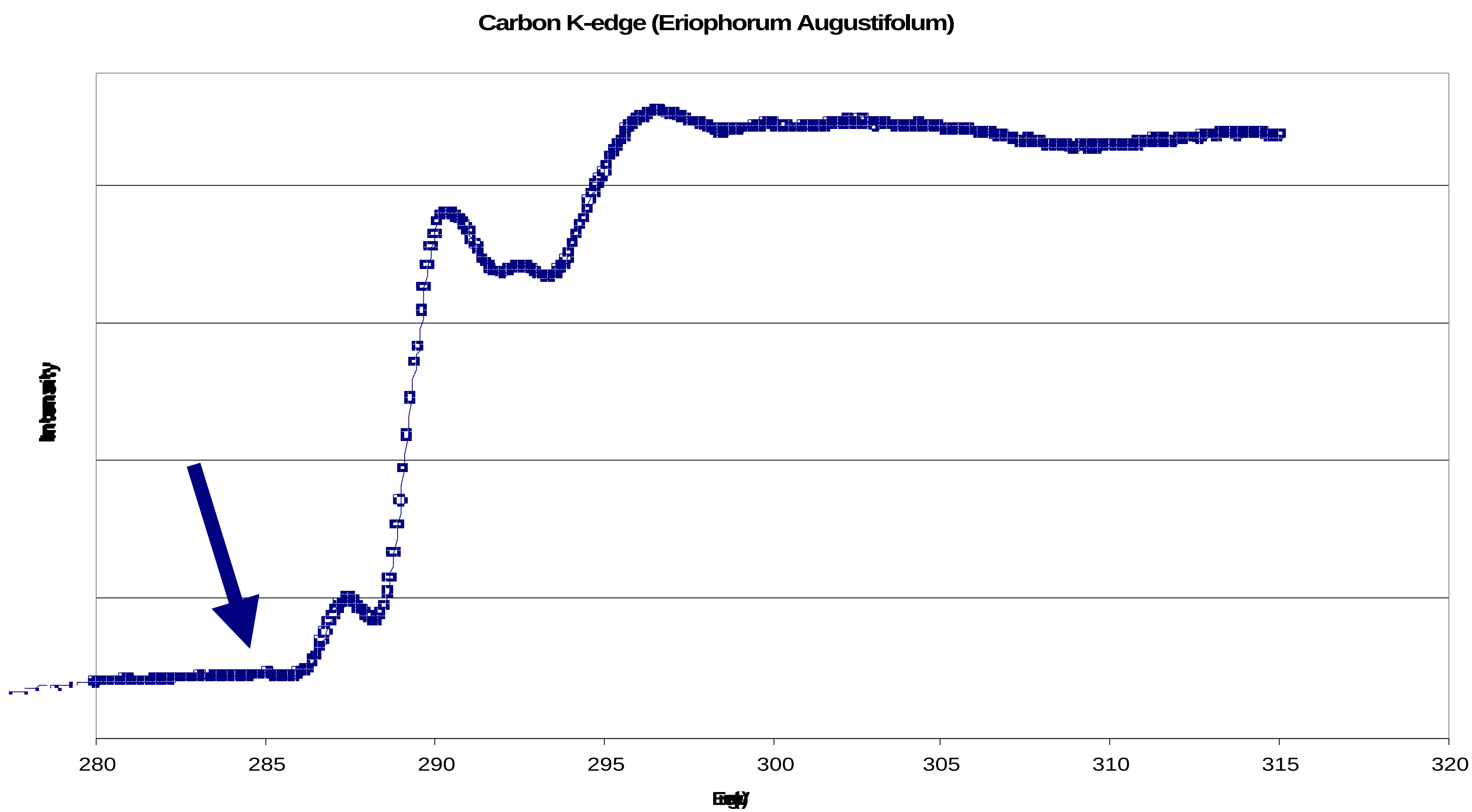
Bulk Data Collection: XANES Spectra of Cellulose and Lignin



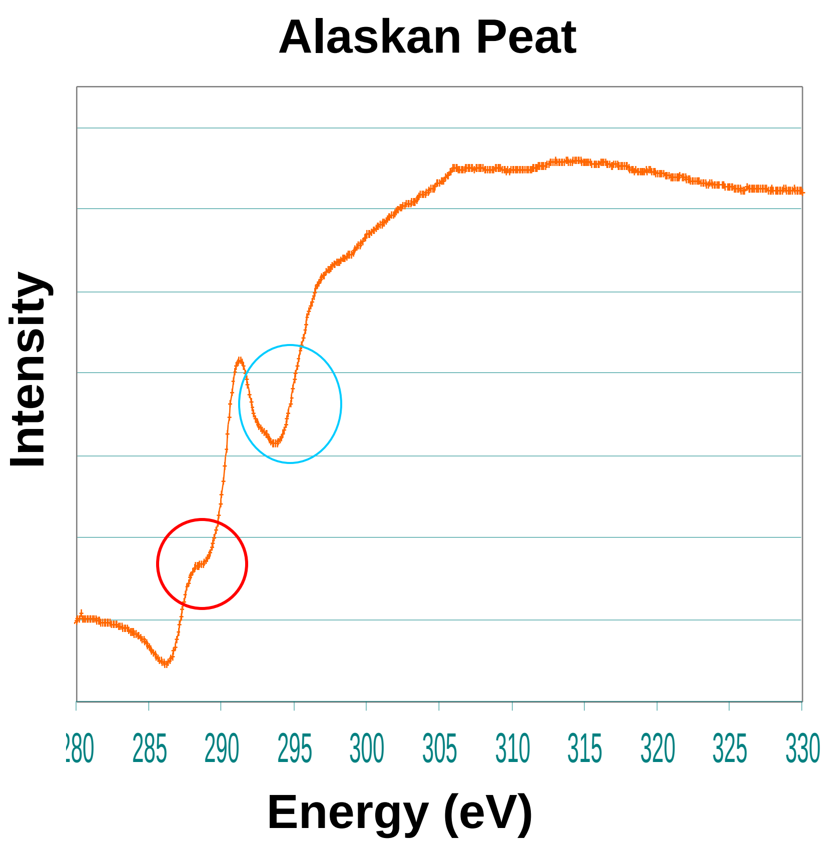
Data Collection: XANES Spectrum of Arctic Peat at the Carbon K-edge

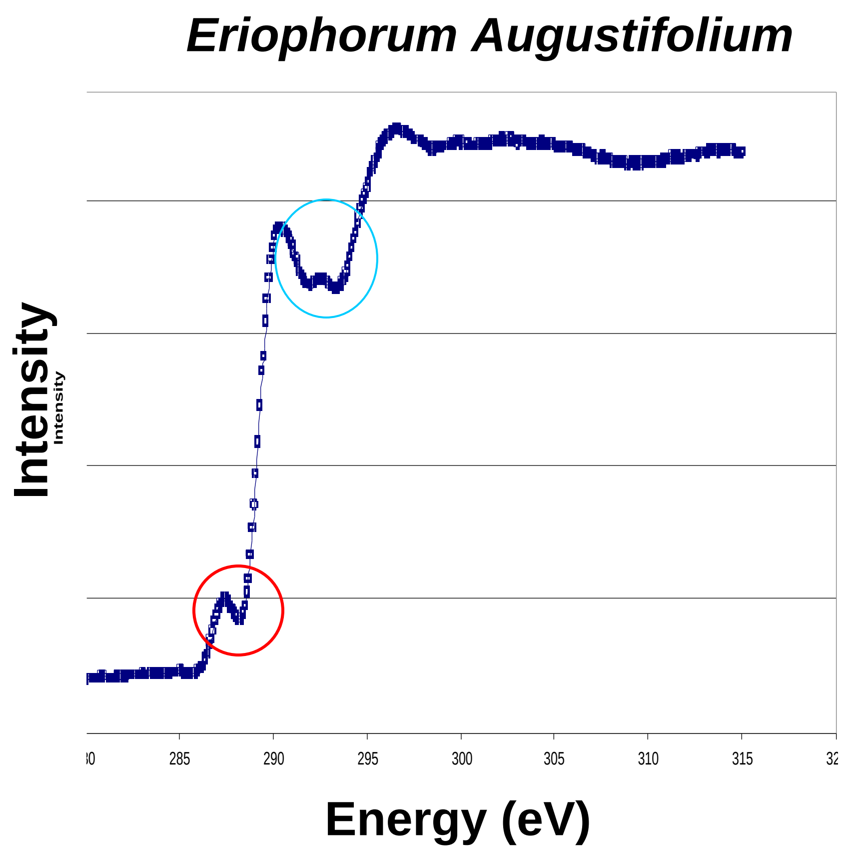


Data Collection: XANES Spectrum of *Eriophorum augustifolum* at the Carbon K-edge



Key Points from XANES Analysis





Sample Preparation: Microscopy

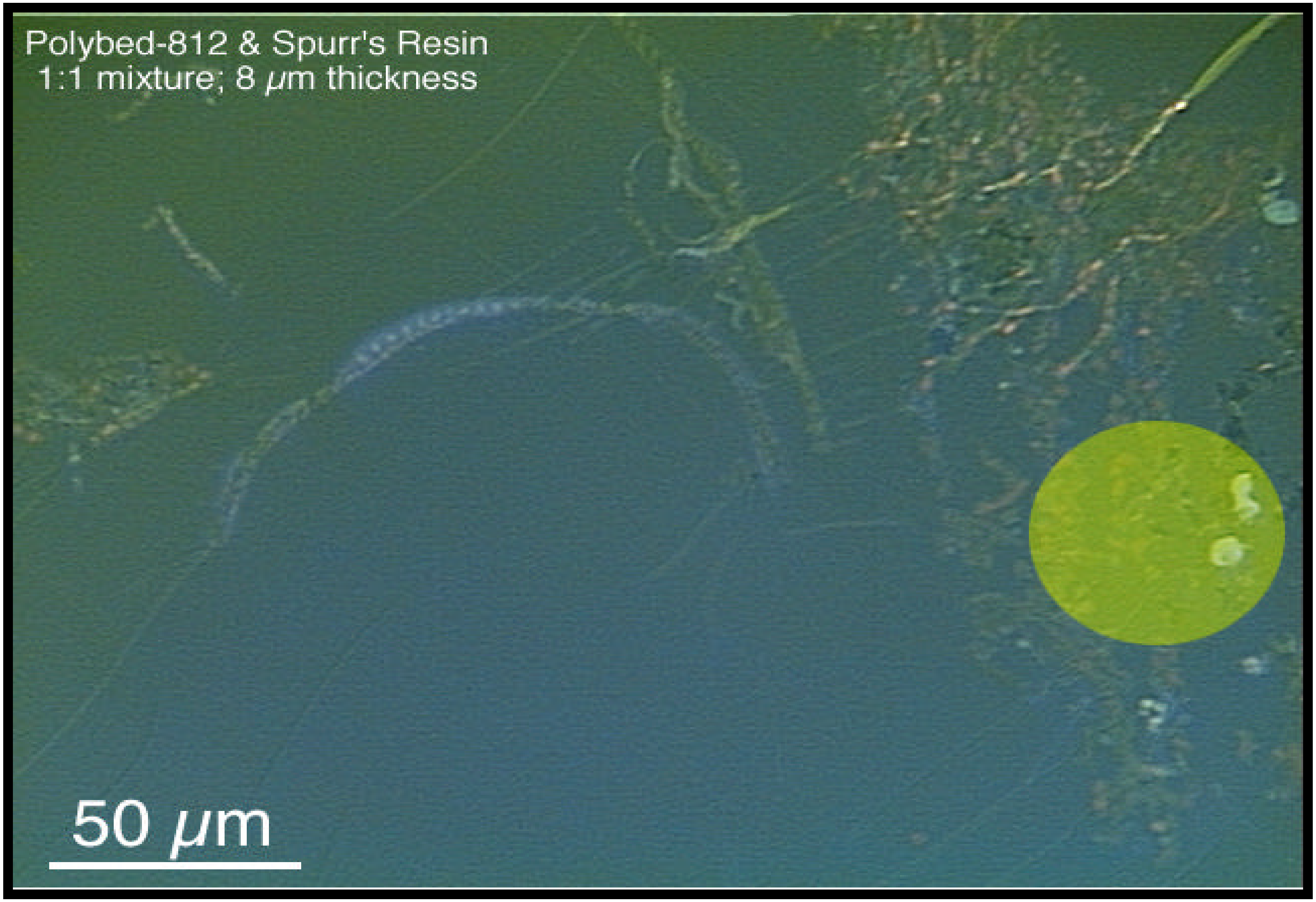
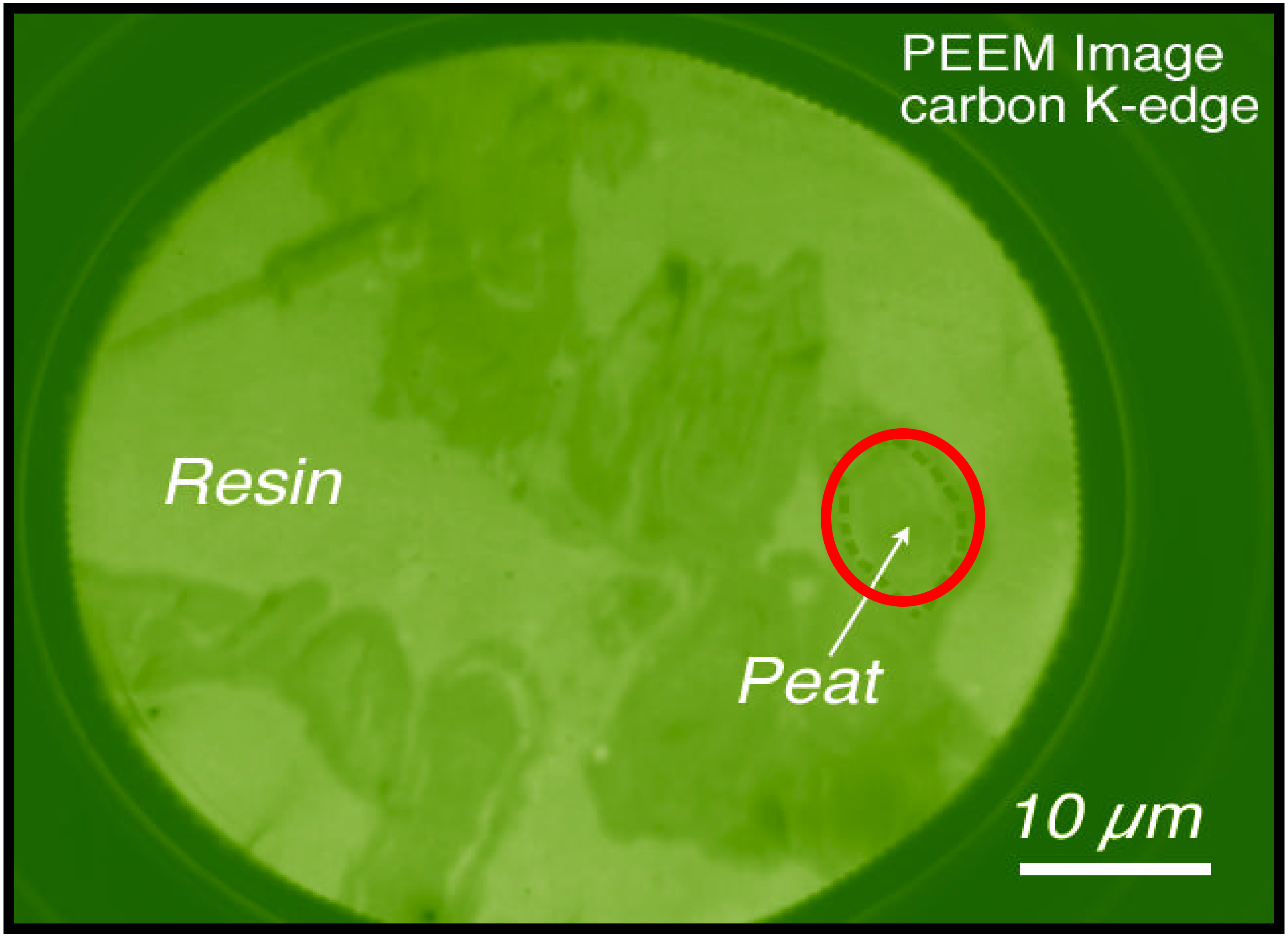
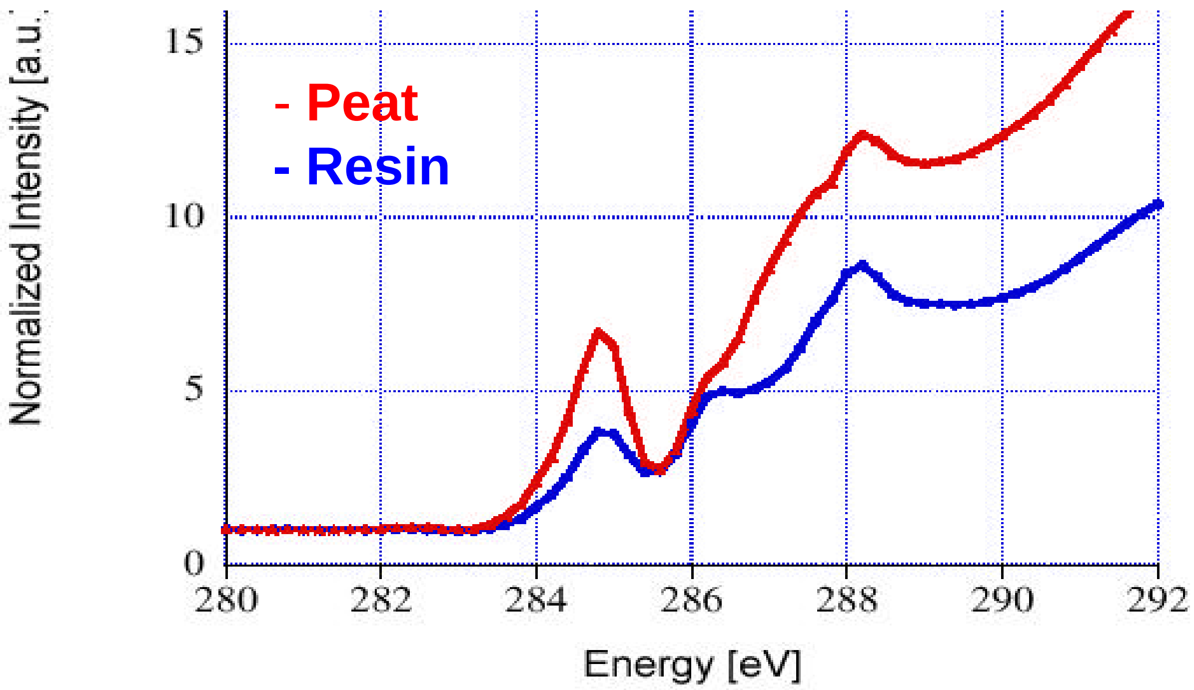


Photo by Russ Spears

Data Collection: PEEM Microscopy



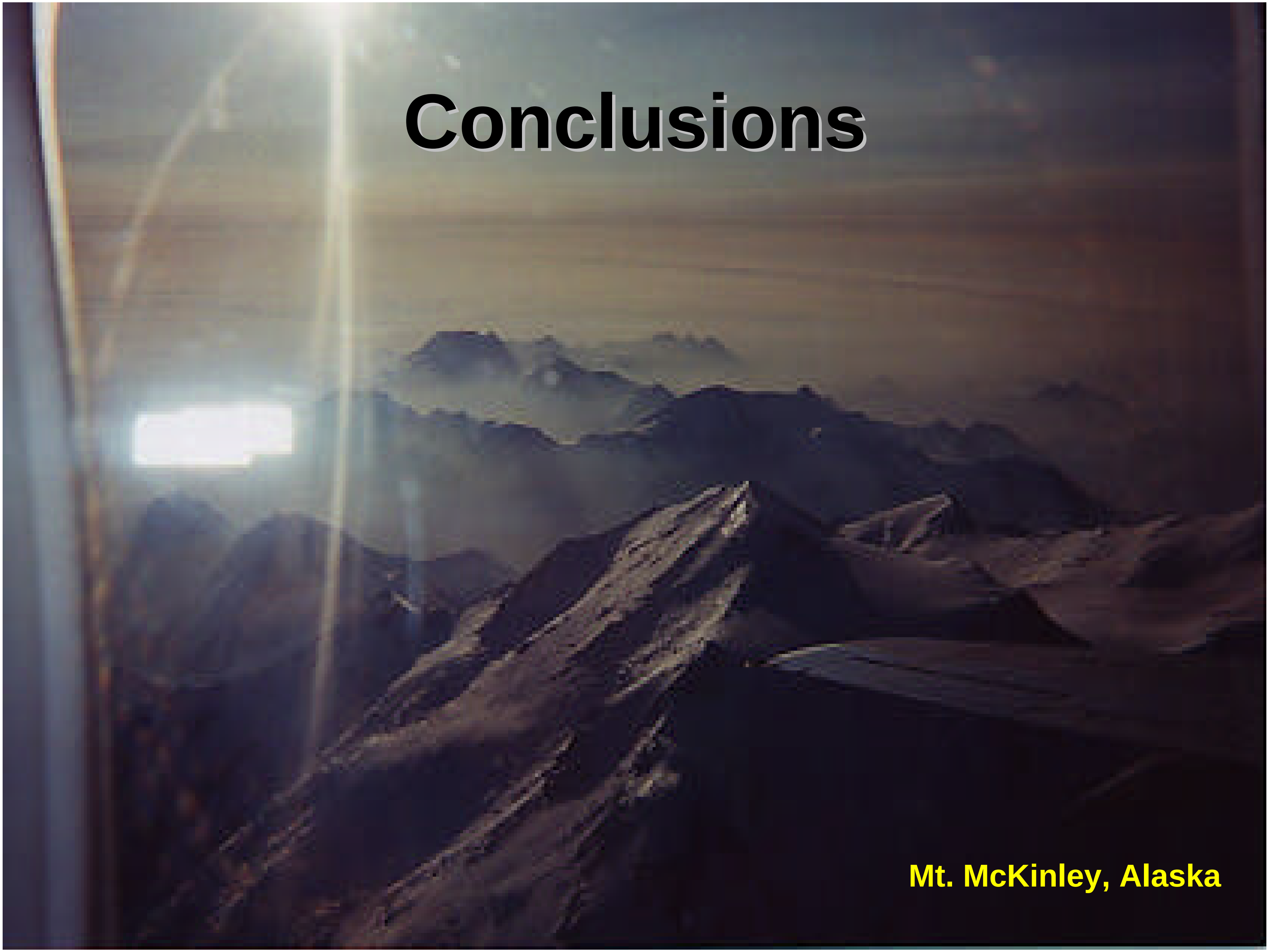
Data Collection: Soft X-ray Microscopy of Isolated Peat Region at the Carbon K-edge



Summary of Preliminary Results

- ❑ Bulk soft x-ray analysis at the carbon K-edge distinguishes between fresh plant material and peat.
- ❑ Chemical microscopy is feasible due to a chemical contrast between embedding resin and peat.
- ❑ Changes in methodology have improved data quality.
- ❑ Chemical microscopy will provide insight into the nature of peat originating from the arctic coastal plain.

Conclusions



Mt. McKinley, Alaska

Future Directions

- Complete bulk spectra of parent vegetation
- Collect bulk and microscopic images at various depth intervals along a peat core
- Utilize IR microscopy techniques
- Analyze and interpret spectra

Acknowledgements

Collaborators:
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- -Dr. DeStassio (SRC)
- -Dr. Xiaoyan Dai (post-doc)
- -Brad Frazier (SRC)

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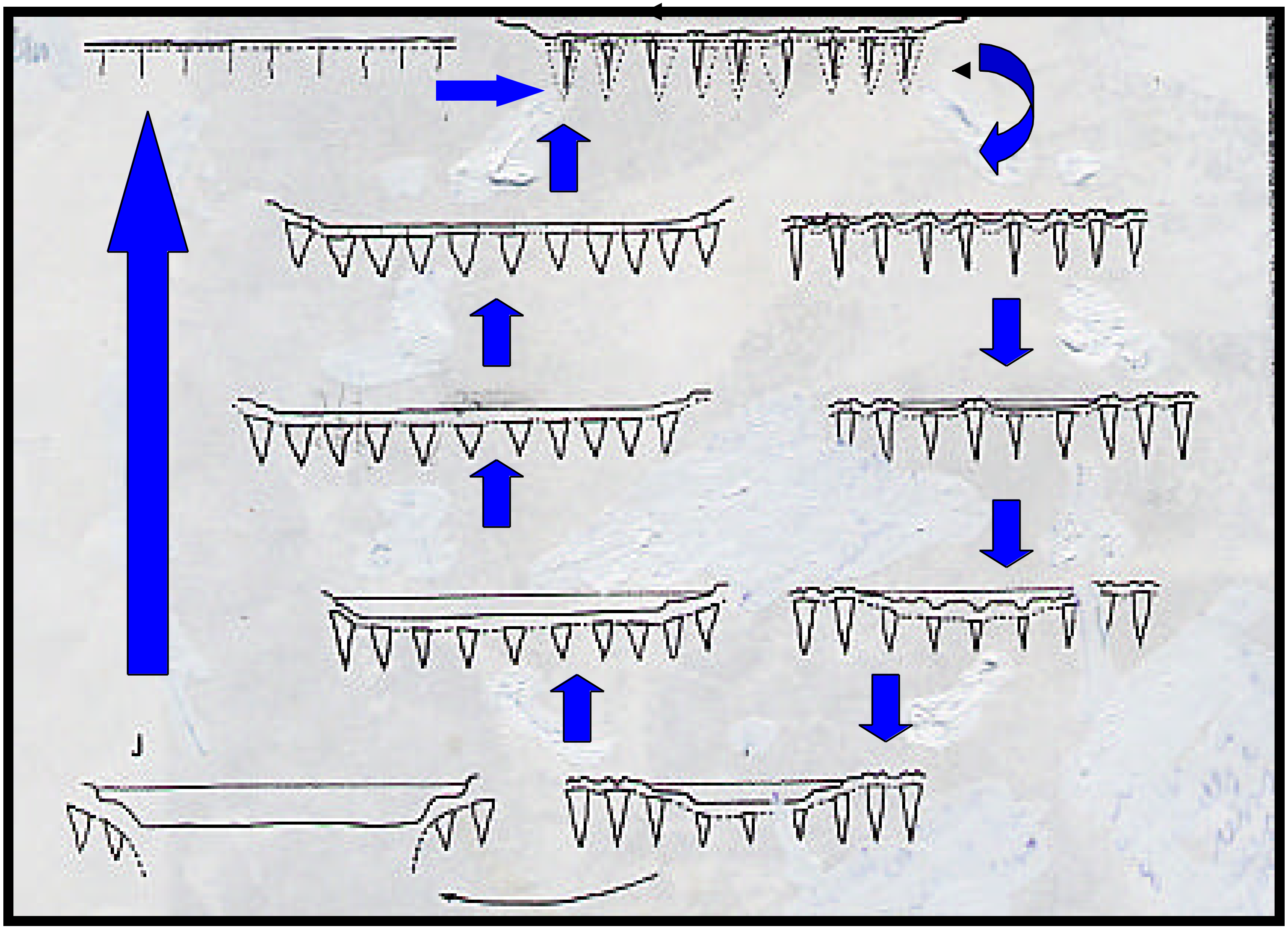
- -Randy Massey (UW-Madison)
- -Dr. Russ Spears (UW-Madison)
- -Dan Wallace (SRC)
- -Adam Hitchcock (SRC)

Other:
- -Barrow Arctic Consortium (BASC)

Arctic Ocean

Background: How Do Thaw Lakes Form?



Billings and Peterson, 1980.

Sample Preparation: Chemical Microscopy

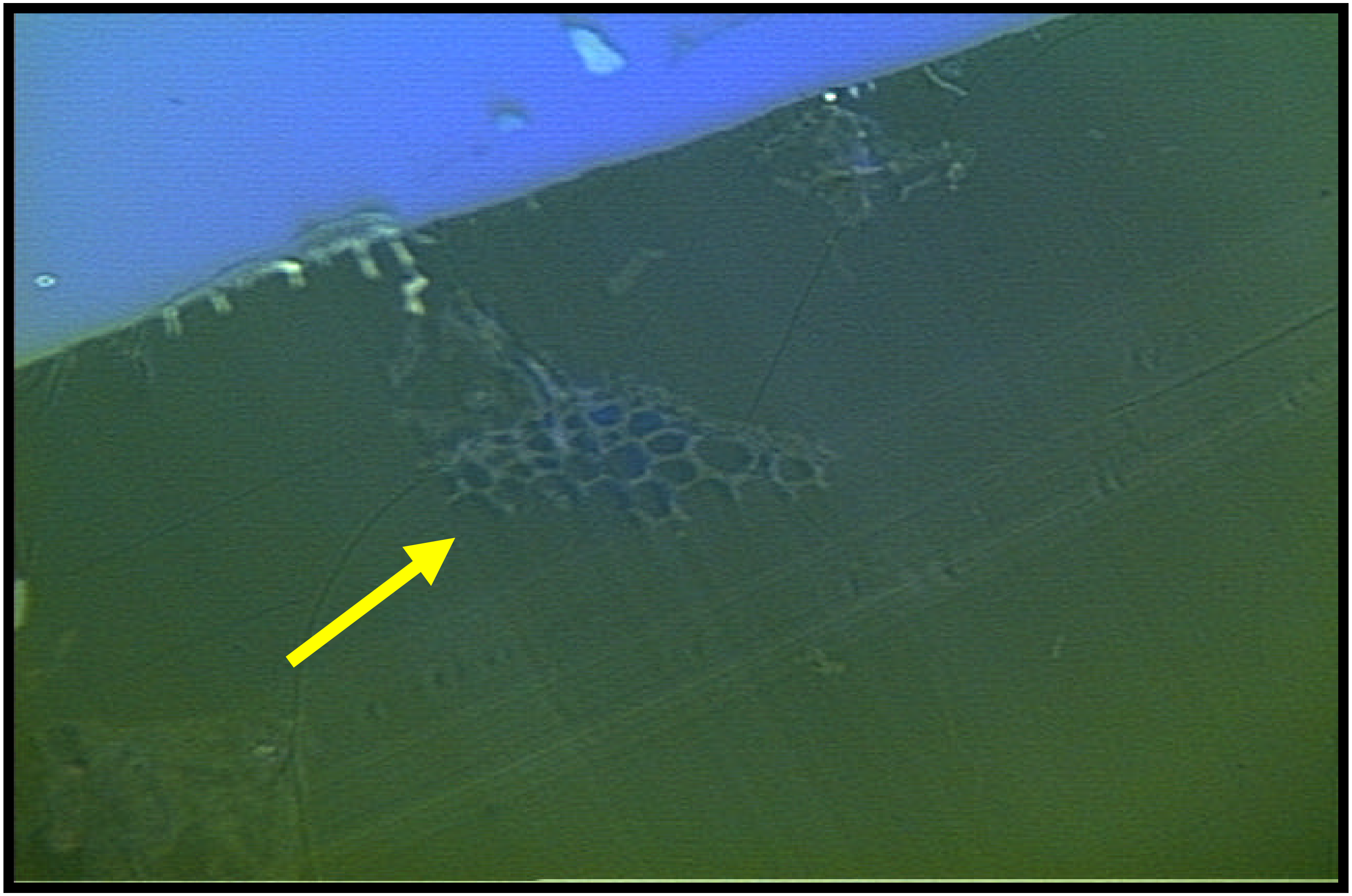
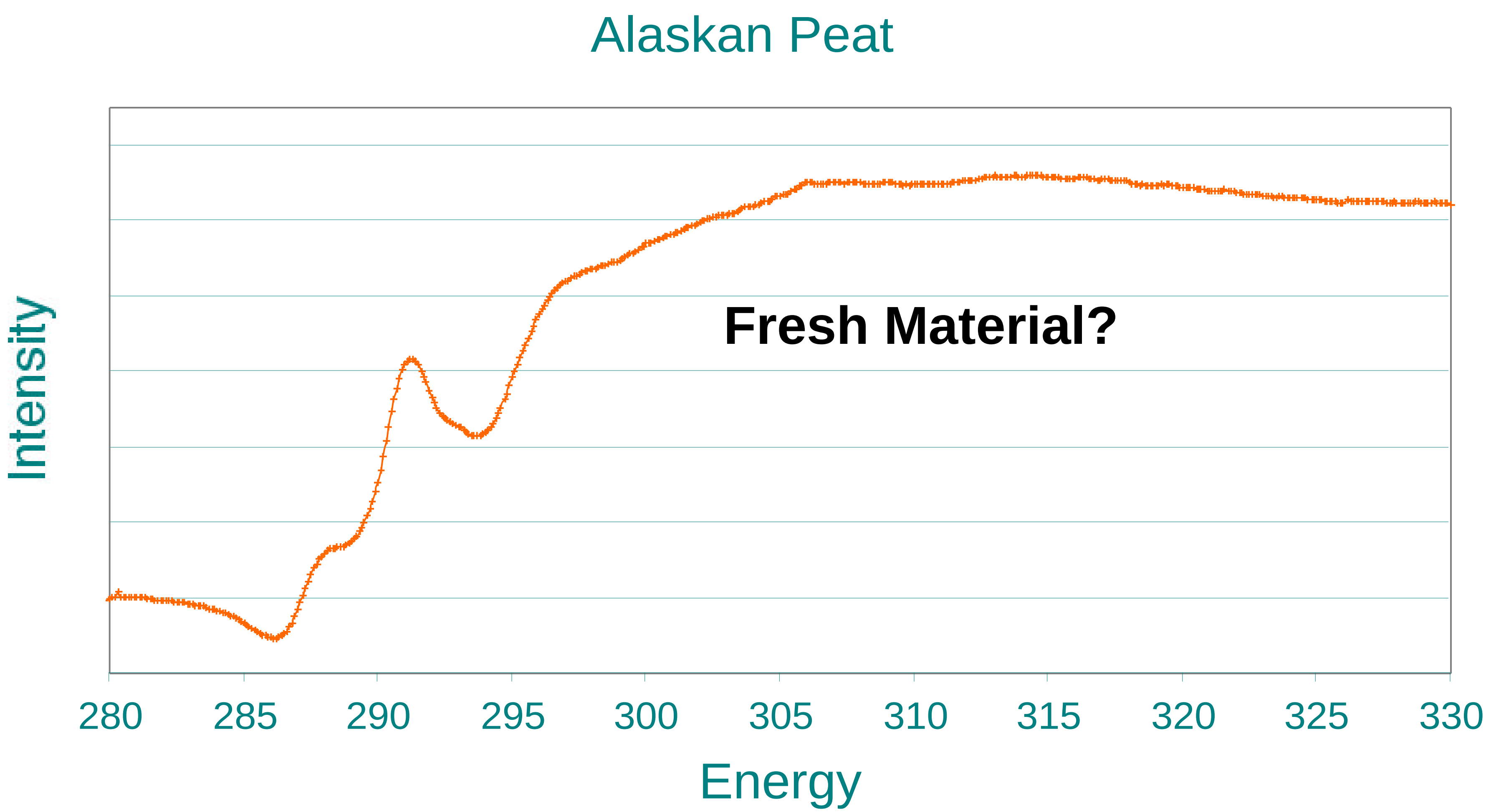


Photo by Russ Spears

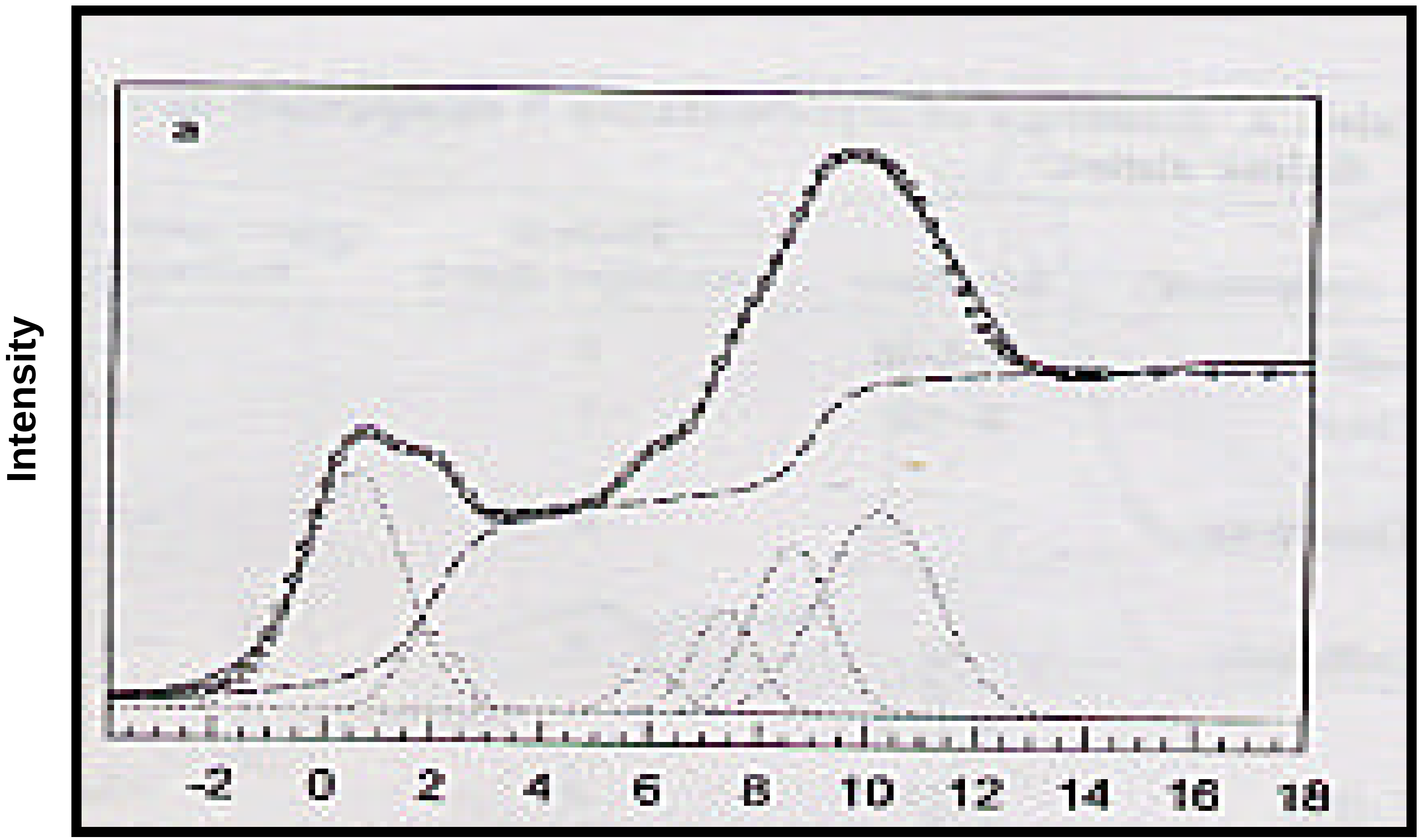
Sample Collection

- **Pollen**
  - proxy for vegetation used in paleoecological research
  - ***Eriophorum scheuzeri, Arctophila fulva, Carex aquatilus***

Data Collection: XANES Spectrum of Arctic Peat at the Carbon K-edge

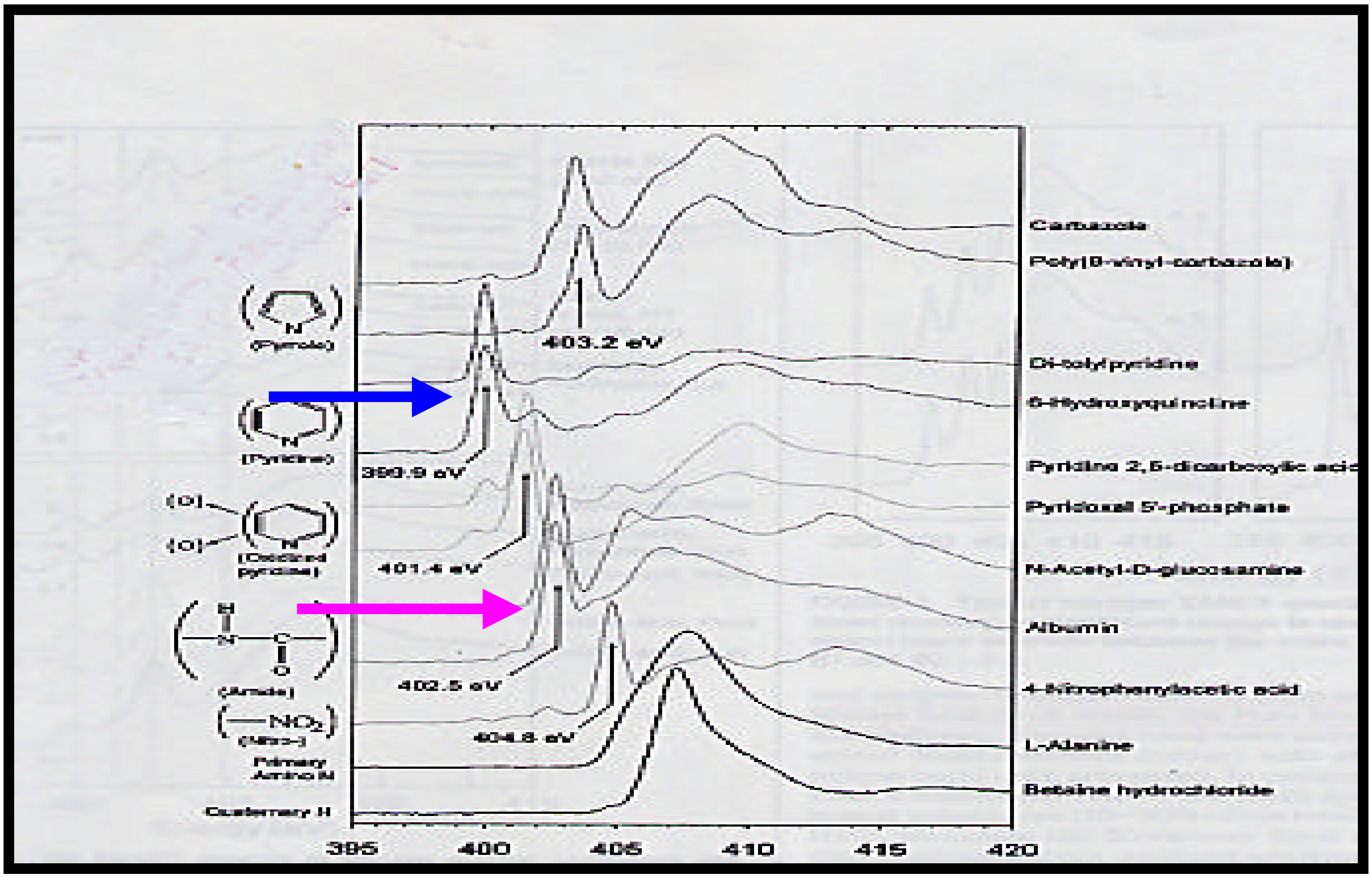


Data Analysis: Peak Deconvolution



Xia et al., 2002

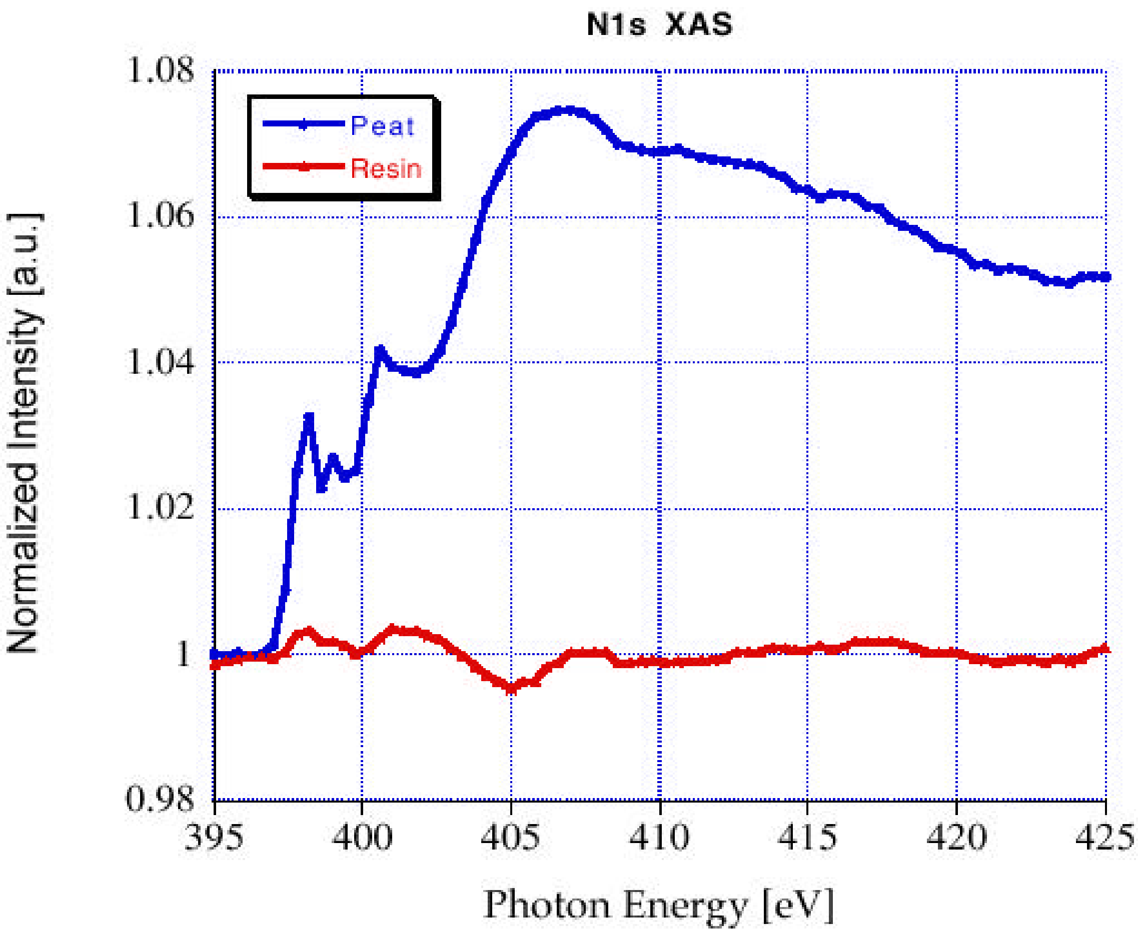
Data Analysis: Peak Assignments with Model Compounds



Energy (eV)

Vairavamurthy et al., 2002

Data Collection: Soft X-ray Microscopy of Isolated Peat Region at the Nitrogen K-edge



Double Normalization

$$\text{Intensity} = \frac{\{(\text{Sample Unknown TEY})(\text{Nickel Mesh})\}}{\{(\text{Silicon Chip TEY})(\text{Nickel Mesh})\}}$$

Fungal Cell Walls

- Chitin
- Cellulose
- Polysaccharides
- Amino sugars

Bacterial Cell Walls

- Lipids
- Lipopolysaccharides & polysaccharides
- Peptidoglycan
- Alkyl macromolecules
- Amino sugars
- ✓ N-acetyl muramic acid

Potential Pitfalls

- **Sample Collection**
  - decomposition may not necessarily increase with depth due to fine root penetration of the peat mat and cryoturbation
- **Data Analysis**
  - difficulty in obtaining quality data, sample charging may limit confidence in our quantification

Other Methods in Peat Characterization

- ❑ Amino sugar analysis (bacterial vs fungal cell wall contributions)
- ❑ Isomer analysis with GC/MS
- ❑ Sulfur XANES – distinguish bacterial cell wall material?
- ❑ Lignin extraction in a mix of humic extracts

Expected Results

- ❑ Relationship between amount of fresh material vs depth/age
- ➢ depth and age may not be linear
- ➢ fresh material vs time may be more appropriate

Research Timetable

2003	2004	2005
-Cell Wall Isolation - Soft X-ray spectroscopy of parent vegetation and cell wall material - Write NSF proposal - Write and submit publication on initial results	-Chem. Microscopy of Peat - **Pollen Isolation and Analysis** -Write and submit publication on those findings - Continued analysis of core peat sample	- Complete thesis publications and defend thesis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